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THE CHEMICAL CONSTITUTION OF NATURAL FATS

By

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PREFACE TO THE SECOND EDITION

THE FIRST EDITION of this book has been out of print for a longer time than could have been wished. As in many other cases, it suffered to some degree by enemy action, whilst production of the present edition has been hindered by the prolonged delays which unavoidably have afflicted the publishing and printing industries during and since the war of 1939–1945. Study of the fats does not appear to have been so much impeded by the prevailing unrest as might have been supposed ; at all events a great deal of new matter has appeared during the six or seven years which have elapsed between the two editions of this book. In consequence it has expanded by about a hundred pages, and in places the story can be presented in a much more complete form than before. Endeavour, not wholly successful, has been made to mention all the more important contributions published before the end of 1945.

The more notable advances (contributed to prominently from the United States and from India, although workers in England, Holland and France have still made opportunities to continue their researches) include the addition of numerous *component acid* data in the groups of land animal and vegetable fats (Chapters III and IV) ; a large number of additional seed fat data have been contributed, and in the animal group the depot fats from a wider range of wild animals have been studied, whilst that of the human species has also been examined. Work on *component glycerides*, although not so extensive, has been notable for the development of methods which enable the more liquid and unsaturated fats to be more adequately investigated, for the more complete development of the glyceride picture in animal depot and milk fats, and for some insight into empirical methods whereby glyceride composition can be roughly predicted from that of the component acids of a fat (Chapters VI and VII). A good deal of fresh information on individual fatty acids (Chapter IX) has been worthy of record, whilst the welcome extended to the discussion of experimental technique has led me to revise and expand Chapter XI, especially in regard to the methods of interpretation of ester-fractions involved in the determination of component acids.

The arrangement of the indexes may have given some trouble to readers of the first edition, and I have endeavoured to make this more clear. The nature of the subject-matter requires treatment by means of several indexes, the use of which will, it is hoped, be facilitated by the indications given on pp. xiii and 529.

Many friends were good enough to give me the advantage of helpful criticism of the first edition, of which I have made much use during the present revision. It is not possible to refer to all who have thus helped me, but amongst them I might mention Professor A. C. Chibnall, F.R.S., Dr. H. Jasperson, Mr. H. M. Langton, Dr. J. A. Lovern, Dr. F. B. Shorland, Mr. P. N. Williams and other colleagues in the Central Research Laboratories at Port Sunlight. In the preparation of the present edition I owe very much to the patient and assiduous help of my colleague, Dr. M. L. Meara, at all stages—

revision, addition, final scrutiny of both manuscript and proofs (in the latter we were also assisted by Mrs. M. L. Meara). I wish to express my appreciative thanks to Dr. Meara, and to all who have given me the benefit of their advice or comments.

T. P. H.

University of Liverpool,
July, 1946.

PREFACE

It has seemed opportune for some time past to write a monograph on the natural fats in such a form that their inter-relationships as a group of naturally occurring organic compounds should be developed as completely as possible, and without primary reference either to their physiological functions or to their technical applications. The many detailed data on the acids combined in natural fats which have been published during the past twenty years or so have made more and more evident the existence of a close connection between the component acids in a fat and its biological source. Therefore, I decided to make some sort of biological classification the basis for the order in which the various natural fats are considered. To those familiar with the more customary sequence of " vegetable fats, animal fats, marine animal fats " the change may seem inconvenient or even unnecessary ; but assurance may be given that contemplation of the fats and their component acids in the sequence developed in Chapters II–IV of this book soon presents itself as the logical and consistent method of approach to their study. This, it is hoped, will be realised by perusal of Chapter I, which is mainly devoted to a general summary of the data discussed in fuller detail in the six chapters which follow.

Whilst acknowledging all responsibility for the method I have adopted, it is right to add that the first use of this principle was made ten years ago by Grün and Halden (*Analyse der Fette und Wachse*, vol. II), who, when describing the usual chemical and physical characteristics of plant and animal fats, arranged them mainly according to their biological origin, in the general order vegetable, marine animal, animal fats. These authors (p. 10) were, however, at that time unable to accept my view that there were sufficient parallelisms between the component acids of seed fats and the families of the parent plants to justify a comprehensive generalisation.

In postponing discussion of the chemical constitution and properties of individual fatty acids until a late stage of the book—indeed, until its main objects have been dealt with—I have followed the example of my friend Dr. G. S. Jamieson, who adopted this plan (I think very usefully) in his "Vegetable Oils and Fats," published in 1932.

The aim has been to include as much as possible of relevant data on the subject published up to the end of 1938, whilst some work which has appeared during 1939 has also been considered. It is hoped that not many investigations have been overlooked which ought to have been mentioned, because one of the chief uses of a volume of this kind should be to stimulate research, to draw the attention of investigators to what has already been done, and to the lacunæ which still exist. For the latter reason, also, some of the more recent work has been discussed more fully than might otherwise have been deemed necessary.

With few exceptions, only those fats whose component acids have been defined in some detail by modern methods are considered in this book. Actually, it will be found that about 420 fats from plant species, about 80 fats from land animals, and about 100 fats of aquatic origin are mentioned ; in several instances these numbers include fats from different parts of the same animal or plant. These figures illustrate on the one hand the disproportion between the number of plant and of animal fats studied, and on the other, that those fats so far adequately studied are drawn from only a minute proportion of the hundreds of thousands of natural species.

I have received much help in the preparation of the book, especially in verifying numerical data and textual references and in correction of proofs from Miss M. Tadman, M.Sc. Dr. M. L. Meara read the book in manuscript and also contributed the part of Chapter X which deals with synthetic glycerides. To these, and to Dr. J. A. Lovern and others with whom I was able to discuss various parts of the work, I offer my warm thanks. I take this opportunity, moreover, to express my great appreciation of my co-workers in this laboratory who, during the past fourteen years, have done very much to encourage and maintain my interest in research on fats by their own keenness and assiduity in the investigations which we have pursued together.

T. P. H.

University of Liverpool.
December, 1939.

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CHAPTER I

INTRODUCTORY SURVEY OF THE NATURAL FATS

THIS book is planned to give as complete an account as possible of the constitution of the fats, and more especially the glycerides, which are produced naturally in plant and animal life. It is intended to treat the natural fats as a group of organic chemical compounds, in exactly the same way as it has been found helpful to have separate monographs dealing with other natural groups such as, for example, the carbohydrates, terpenes, alkaloids, or flavone derivatives. This method of approach is stressed, because it naturally follows that the fats are considered, primarily, neither from the standpoint of their utility as raw materials for any industrial purpose nor with regard to their biochemical functions in the organisms in which they are produced. References will, it is true, be found to these and other aspects in the course of the work; but its first objective is the descriptive presentation of the organic chemistry of the natural fats, so far as our present knowledge takes us.

It is probable that many readers will be already familiar with the subject from the biochemical or the technological side; this circumstance warrants some further explanations. First of all, it will be found that much less reference than usual is made to the many " characteristics " of fats (whether physical, such as density or refractivity, or chemical, such as saponification, acid, iodine or acetyl values, etc.) which have been so widely elaborated and which are indispensable in the routine or rapid characterisation, and even determination, of fatty materials in technical practice. This is, of course, owing to the circumstance that these " characteristics," applied to an entire fat, give in general merely average figures which by no means serve to indicate its detailed composition (although saponification equivalents, iodine values, and occasionally other analytical characteristics, are indispensable in collecting the detailed experimental data upon which knowledge of the chemical structure of fats is ultimately based). The individual fats discussed in this book, with few exceptions, have been investigated so far that the proportions of the separate component acids, and in many cases the chief component glycerides, can be stated with some degree of accuracy; and for the most part the compositions of the fats are given in these forms alone. Many tables illustrating the component acids present in natural fats have been included in the book, and it might have been interesting to have incorporated some of the more important physical and chemical analytical " characteristics " of each fat mentioned. To do so would, however, have greatly increased the size and complexity of these tables (already cumbersome enough). To add separate compilations of the customary analytical characteristics would also have involved considerable increase in the size of the volume and, since full details of the analytical characteristics of individual fats have been collected in a number of excellent technological or general treatises on fats, it seemed unnecessary to repeat them in a work which is primarily a guide to the chemical structure of natural fats and is concerned only with the data relevant thereto.

In the next place, the arrangement of the fats discussed in this volume will doubtless be found unusual. Logically, perhaps, the individual fatty acids, their properties and constitutions, should be discussed before proceeding to their combined forms, the glycerides, etc., whilst the experimental and analytical methods employed in the elucidation of their composition should also precede the essential part of the work. It is a great advantage, on the other hand, to come to the main business of the book as soon as possible; and since, as has been said, most readers are doubtless familiar with the fundamental chemistry of the fatty acids, it has been thought feasible to attempt this. The chapters immediately following therefore deal at once with the component acids and glycerides which have been found to occur throughout the vegetable and animal kingdoms, without undue detail as to the evidence upon which, for example, the constitution of any particular fatty acid is based. Later in the book, however, chapters will be found in which the constitution and specific features of individual fatty acids are considered, and in which accounts are given of the chief experimental and analytical methods referred to in the more general portion of the work. Since the writer has frequently received requests for collected details of various procedures used by his collaborators and himself in the work on fats carried on at the University of Liverpool since 1926, the opportunity has been taken to endeavour to meet these enquiries at the same time. This is the sole reason for describing such technique in what may appear to be exceptional detail: in the various published communications modifications are described from time to time, but it has often not been practicable to include a complete description in any one paper contributed to the scientific journals.

SOME GENERAL CONSIDERATIONS ON THE STUDY OF NATURAL DERIVATIVES OF THE HIGHER FATTY ACIDS

Unanimity has not yet been reached in the terminology to be adopted in classifying the various types of naturally occurring compounds in which higher fatty acids are present. These types are broadly as follows:

(I) *Compounds containing only carbon, hydrogen, and oxygen:*

- (A) Esters of higher fatty acids with glycerol (triglycerides).
- (B) Esters of higher fatty acids with alcohols other than glycerol (higher aliphatic alcohols, sterols, etc.).

(II) *Compounds containing other elements in addition to carbon, hydrogen and oxygen:*

- (C) Esters of glycerol with fatty acids and also phosphoric acid coupled with a nitrogen base.
- (D) Compounds of fatty acids with a carbohydrate and containing nitrogen.
- (E) A few fatty acid derivatives also containing either nitrogen or sulphur.

Even a collective title for the whole group is not completely settled. British workers, following I. Smedley MacLean, referred to the whole group as *lipoids*, the Germans employing the corresponding word (*Lipoide*); but American biochemists adopted Bloor's generic term *lipids*, and at the present time this usage seems to have become general in publications in the English language.

The sub-groups also share several alternative titles, the latter being roughly tabulated as follows:

	British	*German*	*American*
Group Title	Lipoids	Lipoide	Lipids
Sub-group I			Simple lipids
Type A	Fats	Fette	Fats
Type B	Waxes	Wachse	Waxes
Sub-group II	Lipins		Compound Complex lipids
Type C	Phosphatides	Phosphatide	Phospholipids
Type D	Cerebrosides	Cerebroside	Cerebrosides

In the present book the terms used have the following significance :

Lipids. The collective title for the whole group of natural products in which the higher fatty acids are present as essential components (the terms *lipoids* and *lipins* being discarded).

Fats. Natural triglycerides, solid or liquid.

Waxes (type B). These will be most frequently referred to as ester-waxes or, more specifically, as sterol, higher aliphatic alcohol, etc., esters.

Phosphatides. The choline or cholamine salts of the glycerophosphoric acid derivatives of type C above.

Phosphatidic acids. The corresponding free glycerophosphoric acid derivatives of type C (or their metallic salts).

Glycerides are esters of the trihydric alcohol glycerol, in which three fatty acid molecules are combined with one molecule of glycerol. The natural triglycerides or fats are the main concern of the present book. The phosphatides, to which some reference must, however, also be made, are also esters of glycerol, or, more explicitly, are higher acylated esters of a glycerophosphoric acid, usually in the form of a salt with choline or cholamine (β-amino-ethylalcohol)—$C_3H_5(OR')(OR'')(O.PO(OH).B)$, where R′, R″ are higher fatty acid radicals and B is the nitrogen base choline or cholamine.

The constitution of the fats (triglycerides), or for that matter of the ester-waxes or of the phosphatides, may be considered in two distinct ways, namely : (i) with respect to the amounts of the various individual esters present, or (ii) with reference to the proportions of the various *fatty acids* which are present in combination in the natural product as a whole. We may with advantage here confine the discussion to the fats or triglycerides themselves. Very few natural fats have been found to contain only two or even three different acids united with glycerol ; more usually five, six, or seven such acids are present and this number may often be much exceeded. Many common fats, notably milk fats and the fats of fishes, contain a dozen or more component acids. If it were the invariable rule that each natural triglyceride molecule contained only one species of fatty acid (e.g. triolein, tripalmitin), there would be no need for the distinction just mentioned. Expressed on a molar (not weight) percentage basis,* the proportions of component fatty acids and of component glycerides would be the same. Most unfortunately, this is exactly what does *not* happen in nature. As will be seen later, the overwhelming tendency is towards the production of mixed triglycerides,* in which at least two, and often three, species of fatty acids are combined ; simple triglycerides are the exception, and are only produced, apparently, when no other course is open. It therefore follows that the proportions of the component acids in a natural fat, and those of its component glycerides, are by no means the same thing ; and accordingly we have to differentiate at the outset between the *component fatty acids* and the *component glycerides* present in a fat.

---

* The molar composition is frequently more informative than composition by weight in discussing the fats, because it expresses the relative number of molecules of each type of acid, or component glyceride, present in a fat. The difference in the two modes of expression becomes especially significant when fatty acids of widely different molecular weight are present in the same fat. Thus, for instance, the presence of 3 per cent. by weight of butyric acid in the mixed acids of butter fat really means that, out of every 100 mols. of fatty acids, about 10 mols. are butyric acid.

The composition of natural fatty acids being so familiar in the form of weight-percentages, this mode is used to a considerable extent in this book. In many cases, however, it is desirable (as in the milk fats mentioned) to present the facts on a molecular basis of comparison ; and, in some of the quantitative work on component glycerides, this is indeed the only rational course.

Here and there (especially in vegetable seed fats), some natural fats, or fats from a group of biologically related organisms, are found to contain in combination some particular fatty acid which has been found in no other instance in nature ; but this is on the whole decidedly exceptional. The general case is that a number of higher fatty acids occur continually throughout nature. The consequence is that the differences between one fat and another depend very largely on the varying proportions of the fatty acids in combination in the different fats, as well as upon the particular acids which happen to be components. The study of the natural fats is therefore somewhat differently placed from that of many other groups of naturally occurring organic compounds in that it must be conducted on a quantitative, rather than solely upon a qualitative, basis. Accepting the necessity for quantitative treatment of the subject, we may therefore consider, as has already been said, either the proportions of the *component triglycerides* in a fat, or of the *component acids* in the total fatty acids present in combination with glycerol.

A practical difficulty next presents itself : whilst the component acids of a fat or other natural lipid can be determined quantitatively with a considerable degree of accuracy (frequently to within, at all events, one unit per cent. of the total fatty acids), the quantitative determination of the individual component glycerides in a fat is a matter of much greater difficulty. At present, indeed, fats in which the component glycerides have been determined in anything approaching full detail form only a small proportion of those for which we have accurate measures of their component fatty acids. Our knowledge of the individual glycerides present in many natural fats is therefore still far from complete. We have achieved recently a good deal of knowledge of the general build of the mixed glycerides in the more important groups of natural fats, but we cannot yet (except in a very few cases) define the nature and proportion of each individual mixed glyceride present with anything approaching the accuracy with which it is possible to state the total proportions of each fatty acid present in combination in the whole fat.

Fortunately, however, it has now become evident that the mode of union—or interweaving, as it were—of the fatty acids in a natural triglyceride is fundamentally similar over wide areas of both vegetable and animal kingdoms. In other words, the kind and proportions of the individual fatty acids combined in a fat seem to have little influence upon the general mode of construction or assembly of the acids into triglycerides ; the latter are assembled on principles which operate, for the most part, independently of the particular fatty acids which happen to be present.

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* It is unfortunate, from this point of view, to express the composition of a fat (from its detailed fatty acid analysis) as " glycerides of oleic acid," " glycerides of palmitic acid," etc., etc. The only logical and comparable method is to give, in the first place, the component acids as a percentage (wt. or mol.) of the *total fatty acids present.*

On the other hand, the amount and kind of the component fatty acids of natural fats vary extremely widely, whilst, as we shall see, these variations run strikingly parallel in most cases with the biological sources of the materials. A great amount of information becomes available, therefore, by consideration of the composition of the total fatty acids, as distinct from the component glycerides. For the reasons which have already been outlined, the natural fats are considered in detail in this book, first of all, with reference to their *component fatty acids* (Chapters II–IV) and, subsequently, in terms of what is known of their *component glycerides* (Chapters V–VII). Similarly, in endeavouring to present a preliminary survey of the whole field in the present chapter, we shall consider the subject first with reference to the component acids and then with reference to glyceride structure.

THE COMPONENT ACIDS OF NATURAL FATS

Before discussing the fatty acids as found in combination in different groups of organisms, vegetable and animal, a few introductory remarks of a general character on the individual naturally occurring fatty acids appear necessary. To maintain a correct perspective, it is essential to recognise that **oleic acid** (*cis*-Δ^{9}-octadecenoic acid, $CH_3.[CH_2]_7.CH:CH.[CH_2]_7.COOH$) is undoubtedly the most widespread of all natural fatty acids ; in very many fats it forms more than half of the total fatty acids, in relatively few fats does it form less than 10 per cent. of the total fatty acids, and up to the present it has been found absent from no natural fat or phosphatide. The most common constituent of all natural fats is thus an unsaturated (mono-ethenoid), normal aliphatic acid with a content of eighteen carbon atoms and the unsaturated linking between the ninth and tenth carbon atoms of the chain. Many other unsaturated acids, mono- or poly-ethenoid, are also found in fats, and of these quite a number have features of chemical structure which bear similarity, close or remote, to that of oleic acid. Other unsaturated acids, however, seem to be quite different from oleic acid and its structurally related acids in the arrangement of their unsaturated linkings. None of the other unsaturated acids are so uniformly distributed, or so prominent as a whole, in natural fats as oleic acid ; but two at least appear to be nearly as ubiquitous, namely, $\Delta^{9,12}$-octadecadienoic acid (linoleic acid or related forms), $CH_3.[CH_2]_4.CH:CH.CH_2.CH:CH.[CH_2]_7.COOH$, and Δ^{9}-hexadecenoic (palmitoleic, zoomaric) acid, $CH_3.[CH_2]_5.CH:CH.[CH_2]_7.COOH$.

The corresponding saturated normal aliphatic acids are, of course, also widely distributed in natural fats. Here the characteristic member of the group is undoubtedly **palmitic acid,** $CH_3.[CH_2]_{14}.COOH$; this acid occurs prominently in very many fats, in which it may contribute from 15 to 50 per cent. of the total fatty acids whilst, like oleic acid, it is completely absent from extremely few, if any, of the natural fats. Whilst a number of other natural saturated higher fatty acids are found in nature, probably only myristic and stearic acids, $C_{13}H_{27}.COOH$ and $C_{17}H_{35}.COOH$, approach palmitic acid in ubiquity of distribution ; of neither of these, however, can it be said that they are invariably present in natural fats. Stearic acid, of course, is a very familiar acid, and is often erroneously stated to be typical of the natural saturated acids (as oleic undoubtedly is of the unsaturated group). Actually, it is only found in high proportions (25 per cent. or more of the total fatty acids) in the seed fats of a few tropical families of plants

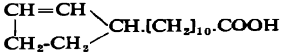
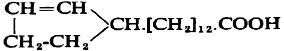
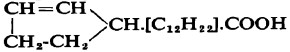
SATURATED ACIDS, $C_nH_{2n}O_2$ or $C_mH_{2m+1}.COOH$

MOLECULAR FORMULA	COMMON NAME	SYSTEMATIC NAME	STRUCTURAL FORMULA
$C_4H_8O_2$	Butyric	*n*-Tetranoic	$CH_3.[CH_2]_2.COOH$
$C_5H_{10}O_2$	*iso*-Valeric	4-Methylbutan-l-oic	$(CH_3)_2.CH.CH_2.COOH$
$C_6H_{12}O_2$	Caproic	*n*-Hexanoic	$CH_3.[CH_2]_4.COOH$
$C_8H_{16}O_2$	Caprylic	*n*-Octanoic	$CH_3.[CH_2]_6.COOH$
$C_{10}H_{20}O_2$	Capric	*n*-Decanoic	$CH_3.[CH_2]_8.COOH$
$C_{12}H_{24}O_2$	Lauric	*n*-Dodecanoic	$CH_3.[CH_2]_{10}.COOH$
$C_{14}H_{28}O_2$	Myristic	*n*-Tetradecanoic	$CH_3.[CH_2]_{12}.COOH$
$C_{16}H_{32}O_2$	Palmitic	*n*-Hexadecanoic	$CH_3.[CH_2]_{14}.COOH$
$C_{18}H_{36}O_2$	Stearic	*n*-Octadecanoic	$CH_3.[CH_2]_{16}.COOH$
$C_{20}H_{40}O_2$	Arachidic	*n*-Eicosanoic	$CH_3.[CH_2]_{18}.COOH$
$C_{22}H_{44}O_2$	Behenic	*n*-Docosanoic	$CH_3.[CH_2]_{20}.COOH$
$C_{24}H_{48}O_2$	Lignoceric	*n*-Tetracosanoic	$CH_3.[CH_2]_{22}.COOH$
$C_{26}H_{52}O_2$	"Cerotic"	*n*-Hexacosanoic	$CH_3.[CH_2]_{24}.COOH$

UNSATURATED ACIDS

Mono-ethenoid acids, $C_nH_{2n-2}O_2$ or $C_mH_{2m-1}.COOH$

MOLECULAR FORMULA	COMMON NAME	SYSTEMATIC NAME	STRUCTURAL FORMULA
$C_{10}H_{18}O_2$		Δ^{9}-Decenoic	$CH_2:CH.[CH_2]_7.COOH$ †
$C_{12}H_{22}O_2$		Δ^{9}-Dodecenoic	$CH_3.CH_2.CH:CH.[CH_2]_7.COOH$ †
$C_{14}H_{26}O_2$		Δ^{5}-Tetradecenoic	$CH_3.[CH_2]_7.CH:CH.[CH_2]_3.COOH$ †
$C_{14}H_{26}O_2$		Δ^{9}-Tetradecenoic	$CH_3.[CH_2]_3.CH:CH.[CH_2]_7.COOH$ †
$C_{16}H_{30}O_2$	Palmitoleic, zoomaric	Δ^{9}-Hexadecenoic	$CH_3.[CH_2]_5.CH:CH.[CH_2]_7.COOH$ †
$C_{18}H_{34}O_2$	Oleic	Δ^{9}-Octadecenoic	$CH_3.[CH_2]_7.CH:CH.[CH_2]_7.COOH$
$C_{18}H_{34}O_2$	Petroselinic	Δ^{6}-Octadecenoic	$CH_3.[CH_2]_{10}.CH:CH.[CH_2]_4.COOH$
✓ $C_{18}H_{34}O_3$	Ricinoleic	12-Hydroxy-Δ^{9}-octadecenoic	$CH_3.[CH_2]_5.CH(OH).CH_2.CH:CH.[CH_2]_7.COOH$ †
$C_{20}H_{36}O_2$	Gadoleic	Δ^{9}-Eicosenoic	$CH_3.[CH_2]_9.CH:CH.[CH_2]_7.COOH$ †
$C_{20}H_{38}O_2$		Δ^{11}-Eicosenoic	$CH_3.[CH_2]_7.CH:CH.[CH_2]_9.COOH$ †
$C_{22}H_{42}O_2$	Cetoleic	Δ^{11}-Docosenoic	$CH_3.[CH_2]_9.CH:CH.[CH_2]_9.COOH$
$C_{22}H_{42}O_2$	Erucic	Δ^{13}-Docosenoic	$CH_3.[CH_2]_7.CH:CH.[CH_2]_{11}.COOH$ †
$C_{24}H_{46}O_2$	Selacholeic, nervonic	Δ^{15}-Tetracosenoic	$CH_3.[CH_2]_7.CH:CH.[CH_2]_{13}.COOH$ †
$C_{26}H_{50}O_2$	Ximenic	Δ^{17}-Hexacosenoic	$CH_3.[CH_2]_7.CH:CH.[CH_2]_{15}.COOH$ †
$C_{30}H_{58}O_2$	Lumequic	Δ^{21}-Tricosenoic	$CH_3.[CH_2]_7.CH:CH.[CH_2]_{19}.COOH$ †

		Mono-ethynoid acid, $C_nH_{2n-4}O_2$ or $C_mH_{2m-3}.COOH$	
$C_{18}H_{32}O_2$	Tariric	$\triangle^{6}$-Octadecynoic	$CH_3.[CH_2]_{10}.C\vdots C.[CH_2]_4.COOH$
		Mono-ethenoid-diethynoid acid, $C_nH_{2n-10}O_2$ or $C_mH_{2m-9}.COOH$	
$C_{18}H_{26}O_2$	Isanic, erythrogenic	Octadeca-$\triangle^{17}$-en-$\triangle^{9,(?11 \text{ or } 15)}$-di-ynoic	$CH_2:CH.C\vdots C.[CH_2]_4.C\vdots C.[CH_2]_7.COOH$ † or $CH_2:CH.[CH_2]_4.C\vdots C.C\vdots C.[CH_2]_7.COOH$ †
		Cyclic unsaturated acids, $C_nH_{2n-4}O_2$ or $C_mH_{2m-3}.COOH$	
$C_{16}H_{28}O_2$	Hydnocarpic	11-$\triangle^{2}$-Cyclopentenyl-*n*-undecanoic	
$C_{18}H_{32}O_2$	Chaulmoogric	13-$\triangle^{2}$-Cyclopentenyl-*n*-tridecanoic	
$C_{18}H_{30}O_2$	Gorlic	13-$\triangle^{2}$-Cyclopentenyl-$\triangle^{6:7}$-tridecenoic	
		Di-ethenoid acids, $C_nH_{2n-4}O_2$ or $C_mH_{2m-3}.COOH$	
$C_{18}H_{32}O_2$	Linoleic	$\triangle^{9,12}$-Octadecadienoic	$CH_3.[CH_2]_4.CH:CH.CH_2.CH:CH.[CH_2]_7.COOH$ †
$C_{19}H_{34}O_2$		12-Methyl-$\triangle^{9,11}$-Octadecadienoic (?)	$CH_3.[CH_2]_5.C(CH_3):CH.CH:CH.[CH_2]_7.COOH$ †
		Tri-ethenoid acids, $C_nH_{2n-6}O_2$ or $C_mH_{2m-5}.COOH$	
$C_{16}H_{26}O_2$	Hiragonic	$\triangle^{6,10,14}$-Hexadecatrienoic	$CH_3.CH_2.CH:CH.CH_2.CH:CH.[CH_2]_2.CH:CH.[CH_2]_4.COOH$
$C_{18}H_{30}O_2$	Linolenic	$\triangle^{9,12,15}$-Octadecatrienoic	$CH_3.CH_2.CH:CH.CH_2.CH:CH.CH_2.CH:CH.[CH_2]_7.COOH$ †
$C_{18}H_{30}O_2$		$\triangle^{6,9,12}$-Octadecatrienoic	$CH_3.[CH_2]_4.CH:CH.CH_2.CH:CH.CH_2.CH:CH.[CH_2]_4.COOH$
$C_{18}H_{30}O_2$	Elæostearic	$\triangle^{9,11,13}$-Octadecatrienoic	$CH_3.[CH_2]_3.CH:CH.CH:CH.CH:CH.[CH_2]_7.COOH$ †
$C_{18}H_{28}O_3$	Licanic	4-Keto-$\triangle^{9,11,13}$-Octadecatrienoic	$CH_3.[CH_2]_3.CH:CH.CH:CH.CH:CH.[CH_2]_4.CO.[CH_2]_2.COOH$ †
		Poly-ethenoid acids	
		(i) TETRA-ETHENOID	
$C_{16}H_{24}O_2$		Hexadecatetraenoic	
$C_{18}H_{28}O_2$	Parinaric	$\triangle^{9,11,13,15}$-Octadecatetraenoic	$CH_3.CH_2.[CH:CH]_4.[CH_2]_7.COOH$ †
$C_{18}H_{28}O_2$	Stearidonic	Octadecatetraenoic	
$C_{20}H_{32}O_2$	Arachidonic	$\triangle^{5:8,11,14}$-Eicosatetraenoic	$CH_3.[CH_2]_4.CH:CH.CH_2.CH:CH.CH_2.CH:CH.CH_2.CH:CH.[CH_2]_3.COOH$
(?) $C_{22}H_{36}O_2$		Docosatetraenoic	
		(ii) PENTA-ETHENOID	
$C_{20}H_{30}O_2$		Eicosapentaenoic	
$C_{22}H_{34}O_2$	" Clupanodonic "	Docosapentaenoic	
$C_{26}H_{42}O_2$	Shibic	Hexacosapentaenoic	
		(iii) HEXA-ETHENOID	
$C_{22}H_{32}O_2$		Docosahexaenoic	
$C_{24}H_{36}O_2$	Nisinic	Tetracosahexaenoic	
$C_{26}H_{40}O_2$	Thynnic	Hexacosahexaenoic	

The structural formulæ of the unsaturated acids to which a † is attached indicate that such acids possess one or more points of constitutive resemblance to oleic acid.

and in the depot fats of some land animals; its prominence in ox and sheep depot fats doubtless caused the impression that it was as abundant in nature as oleic acid.*

It should be added here that with the solitary exception of *iso*valeric acid (found only in the depot fats of the dolphin and porpoise), the molecules of all natural straight-chain fatty acids, saturated or unsaturated, contain an even number of carbon atoms. It may also be mentioned that, when one saturated acid is present in fairly large amount, subsidiary proportions of the natural saturated acids next higher and lower in the homologous series are often also observed. Thus, just as myristic and stearic acids are usually present in subsidiary amounts when palmitic is a major component acid, so, in those tropical seed fats in which, as mentioned, stearic acid is prominent there is also almost always a small amount of arachidic acid, $C_{19}H_{39}.COOH$, as well as palmitic acid.

The chief acids found, as major or minor components, in natural fats are listed on pp. 6–7 to facilitate reference in the remainder of this chapter. Further details of their chemical constitution or special properties will be found in Chapter IX.

The list of naturally occurring acids as given above is not a complete one; thus, for example, isomeric dodecenoic and tetradecenoic acids have been encountered in a few specific seed fats and, again, it is not yet possible to give an accurate statement of the natural polyethenoid fatty acids. All the acids which will necessarily be mentioned in what follows in this chapter have, however, been included.

Having cleared the ground by the explanatory matter in the preceding pages, we can now proceed to consider, from a broad point of view, the distribution of fatty acids in the numerous varieties of natural fats. As will be already evident, the proportion of any single acid in the total acids of a fat is widely variable, sometimes very great, in other cases quite small. It is convenient to group the acids of any fat into two rough categories: *major component acids* and *minor component acids*. As employed by the writer, these terms are not interpreted by any means rigidly; a "major component acid" is defined as one which may form anything from about 10 per cent. upwards of the total fatty acids combined in a fat. At first glance, of course, a constituent contributing only 10 per cent. of the whole may appear misnamed as a "major" component; but when it is remembered that many fats include ten or more different acids in their glycerides it will be seen that the presence of one acid to the extent of more than about 10 per cent. frequently means that it may be one of several chief components.

The chief utility of roughly sorting out the component acids of fats into these two groups is that we then perceive at once that, in very many instances, fats from organisms which have been classed together from morphological and anatomical considerations by biologists share the same fatty acids as major components; so that we reach the important conclusions that natural fats may to a large extent be classified according to their major component acids, and that such a grouping follows fairly closely that already developed from biological considerations for the parent organisms. Although such classification of natural fats rests chiefly on their major component acids, there are quite a number of cases wherein a minor component acid is as characteristic as the major components for a particular group of fats. This is not so general as the relationships observed in the major component acids of most fats, but is in some cases of importance in defining the similarities in one or other group. The minor component acids which are thus, as it were, as definitely characteristic of a natural fat-group as some of the major components are, for the most part, those acids which (either as major or minor components) pervade the whole range of natural fats. Two simple instances may be given. In seed fats of the families Cruciferæ, Umbelliferæ, and some others palmitic acid (which is in most fats a " major component " forming 10 per cent. or more of the total fatty acids) only amounts to 2–3 per cent. of the total fatty acids, but it is found quite regularly in this proportion in different seed fats of these families and is clearly a characteristic, although a minor, component of the fats in question. Similarly, hexadecenoic acid, which is relatively abundant in fats of aquatic origin, is present as a definitely minor, but quite characteristic, component of the depot and the milk fats of the higher land mammals, where it amounts to only about 3 per cent. of the total fatty acids.

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* Boekenoogen[7] has statistically surveyed the distribution of fatty acids in world-wide commercial vegetable fats. From his calculations it would appear that the percentage distribution of each fatty acid is as follows: oleic 34, linoleic 29, palmitic 11, lauric 7, linolenic 6, myristic 3, erucic 3, stearic 3, and all others 4 per cent. Whilst these data cannot be taken as valid for the complete range and output of seed and fruit coat fats, and do not take into account the fats produced in aquatic and land animals, they are of interest as an illustration of the general trend of specific fatty acid production in a sector of the vegetable kingdom.

It has been the custom, in treatises on this subject, to commence the descriptive account of natural fats with those of the seeds produced by vegetable plants—probably because of frequent relative simplicity in the component fatty acid mixtures encountered in this group. The detailed data which have been gathered in steadily increasing numbers during the past quarter of a century have emphasised the fact, already mentioned, that natural fats tend to align themselves, by their component acids, in groups according to their biological origin, and have also revealed that, to put the matter in a few words, the fats of the simplest and most primitive organisms are usually made up from a very complex mixture of fatty acids whilst, as biological development has proceeded, the chief component acids of the fats of the higher organisms have become fewer in number. In the animal kingdom this change in type is remarkably progressive and culminates, in the depot fats of the higher land mammals, in fats in which oleic, palmitic and stearic acids are the major components. In vegetable seed fats, as a rule, similar simplicity is seen in the major component acids but here, in a number of families, fatty acids are found which apparently occur nowhere else in nature.

This sequence of characteristics in the natural fats was remarked upon by the writer in 1934–1935 in a Jubilee Memorial Lecture to the Society of Chemical Industry,[1] and it was suggested that " perhaps, when in the course of time sufficiently wide and detailed data have been collected, systematic description of the natural fats will commence with those of the minute aquatic flora and fauna, will proceed to those of the larger aquatic denizens, and then to the two respective branches of land flora and land fauna." Since this statement was made, further data have been published, notably on the fats of primitive aquatic organisms, on those of some amphibia and reptiles, and on the minor characteristic components of those of some herbivorous mammals, all of which add to the force of the argument that the logical sequence of a descriptive account of the natural fats is to take them, as nearly as may be, in the order of biological development of their parent organisms.

The chapters which immediately follow are therefore devoted, in that order, to detailed accounts of the component acids of the fats of aquatic flora and fauna, of land animals, and of land plants. In the next few paragraphs we proceed to give, from this standpoint, a brief general survey of natural fats.*

Component acids of fats of aquatic origin. All fats of aquatic origin contain a typically wide range of combined fatty acids, mainly of the unsaturated series. The unsaturated acids include those containing 16, 18, 20, and 22 carbon atoms in the molecule (conveniently referred to as unsaturated C_{16}, C_{18}, C_{20}, and C_{22} acids) in varying, but major proportions and in different states of unsaturation; the only major component saturated acid is palmitic acid (usually 10–18 per cent. of the total acids). Myristic and stearic acid (the latter not exceeding 1–2 per cent.) are often present in minor proportions, as also may be unsaturated C_{14} and even C_{24} acids. The proportions of the major component unsaturated acids vary considerably, however, in the fats of different kinds of marine organisms.

Perhaps the most prominent differences are in the component fatty acids of fats from sea-water life on the one hand and fresh-water life on the other. In fats from all fresh-water life, plant or animal, small or large, the type appears to be much the same, the component acids being relatively rich in unsaturated C_{16} and C_{18} acids, with low contents of those of the C_{20} and C_{22} series (the latter often being minimal); the unsaturated C_{16} acids frequently form 30 per cent. or more of the total fatty acids. Whilst the relative proportions of the four groups of unsaturated acids are of the same order throughout all fats from fresh-water flora or fauna so far studied, minor differences are noticeable in the degree of unsaturation, and also in the extent to which the acids are combined with higher fatty alcohols or glycerol-alcohol ethers (selachyl, chimyl, or batyl alcohols, *cf.* p. 31) in the form of wax esters, in addition to the glycerides (which usually predominate).

In the marine world, on the other hand, definite differences from the fresh-water type are often to be observed. The fats of marine diatoms and of green marine algæ are of the fresh-water type in instances so far studied, but those of red and brown marine algæ show differences in the relative proportions of the various homologous unsaturated members. Also, the fats of marine plankton Crustacea (which feed on the diatoms) are considerably different from that of their food—unsaturated C_{16} and C_{18} acids are reduced in amount and C_{20}, and especially C_{22}, acids are correspondingly increased. This crustacean fat type persists as a general background throughout almost the whole range of marine fish and mammalia, although it may again be modified in certain families in various ways. In Elasmobranch fish, for example, the triglycerides are often accompanied by abnormal proportions of non-fatty compounds, including especially the hydrocarbon squalene and sometimes the glycerol ether-esters already mentioned. When these substances are also produced in quantity it has invariably been found that the unsaturation of the acids in the triglycerides is almost wholly mono-ethenoid, while in addition definite proportions (up to 10 per cent.) of a mono-ethenoid C_{24} acid, selacholeic acid, have also been frequently observed in these cases. In other families of Elasmobranchs another type of fat is found, characterised by very low proportions of non-glyceridic esters and extremely high unsaturation in the C_{22} and C_{20} acids, which may be present in larger quantities than in the previous type.

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* This general outline is, for the most part, an amplification of an article contributed to *Nature* by Dr. J. A. Lovern and the present writer in 1936.[2]

Similar specific variations in the component acids of fats of the more developed marine fish and mammalia include the elaboration of esters of higher alcohols as well as triglycerides in depot fats of the Physeteridæ (sperm whales) (here, again, the unsaturation of the acids present is abnormally low), and that of mixed glycerides of the quite exceptional *iso*valeric acid in those of the Delphinidæ (porpoise, etc.) ; such differences are as definitely characteristic as those in the anatomical features of the respective groups. Other interesting marine animal fats include those of the sturgeon, which are of the fresh-water type ; while salmon body fats alter progressively as the fish develop from purely fresh-water to marine animals.

Component acids of fats of land animals. As we pass from depot fats of aquatic to those of land animals we find marked simplification in the mixed fatty acids, and in the higher land animals the important component acids are almost always the (mono-ethenoid) oleic, $C_{18}H_{34}O_2$, and the (saturated) palmitic, $C_{16}H_{32}O_2$, the latter occurring in much larger proportions than in aquatic animal fats, namely, about 25–30 per cent. of the total fatty acids —a figure which is roughly the same for the depot fats of widely different animals such as the rat, rabbit, kangaroo, cat, pig, sheep, ox, reindeer, horse, bear, lion, man, and also, usually, birds. Nevertheless, the disappearance of the characteristic " aquatic " unsaturated acids of the C_{16} (mainly mono-ethenoid, hexadecenoic), C_{18}, C_{20}, and C_{22} (mono- and poly-ethenoid) series is by no means abrupt.

In depot fats of amphibians and reptiles, unsaturated C_{16}, C_{20}, and C_{22} acids are present, but in less amount than in fish depot fats : frog depot fat contains 15 per cent. of hexadecenoic and the same amount of unsaturated C_{20-22} acids, that of the lizard 10 per cent. of the C_{16}, and 5 per cent. of the C_{20-22} acids ; the unsaturation of the C_{20} and C_{22} acids, though still high, is not so pronounced as in the fish oils. In these fats the proportion of saturated acids is not very different from that in " aquatic " fats, and the drop in unsaturated C_{16}, C_{20}, and C_{22} acids is balanced chiefly by increase in unsaturated C_{18} (mainly oleic) acid. In the depot fats of rats and of the domestic fowl, again, there occur small quantities (6–8 per cent.) of hexadecenoic acid and minor amounts (0·5–1 per cent.) of unsaturated C_{20} and C_{22} acids. The latter acids were already known, from the work of J. B. Brown and his colleagues, to be present in very small proportions in other animal depot fats (for example, pig) and in cow milk fat. In rats, rabbits, and hens, in contrast to the frog, lizard, and tortoise, the saturated acids of the depot fats form 30–35 per cent. of the total acids (palmitic, 25–28 per cent.).

This progressive alteration in the kinds of fatty acid present in the glycerides of different types of animals is more clearly seen if a table is drawn up giving the general range of values so far observed for the main component acids in some of the groups of the larger animals. (*See next page.*)

Almost all the acids other than palmitic (that is, about 70 per cent. of the

COMPONENT ACIDS (PERCENTAGE WT.) IN ANIMAL DEPOT FATS

<table>
<tr><th></th><th>Saturated</th><th colspan="4">Unsaturated</th></tr>
<tr><th></th><th>Palmitic</th><th>C_{16}
(Hexadecenoic)</th><th>C_{18}</th><th>C_{20}</th><th>C_{22}</th></tr>
<tr><td>Fish, fresh-water</td><td>13–15</td><td>ca.20</td><td>40–45</td><td>ca.12</td><td>0–5</td></tr>
<tr><td>,, marine</td><td>12–15</td><td>15–18</td><td>27–30</td><td>20–25</td><td>8–12</td></tr>
<tr><td>Whales</td><td>12–15</td><td>15–18</td><td>35–40</td><td>15–20</td><td>5–10</td></tr>
<tr><td>Frog</td><td>11</td><td>15</td><td>52</td><td colspan="2">15</td></tr>
<tr><td>Tortoise</td><td>14</td><td>9</td><td>65</td><td colspan="2">7</td></tr>
<tr><td>Lizard</td><td>18</td><td>10</td><td>56</td><td colspan="2">5</td></tr>
<tr><td>Domestic fowl</td><td>25–26</td><td>6–7</td><td>ca.60</td><td colspan="2">0·5–1</td></tr>
<tr><td>Rat</td><td>24–28</td><td>7–8</td><td>ca.60</td><td colspan="2">0·3–0·5</td></tr>
<tr><td>Kangaroo</td><td>25</td><td>3</td><td>48</td><td colspan="2">3</td></tr>
<tr><td>Cat</td><td>29</td><td>4</td><td>43</td><td colspan="2">Trace</td></tr>
<tr><td>Pig</td><td>25–29</td><td>2–3</td><td>50–65</td><td colspan="2">0·3–1</td></tr>
<tr><td>Ox</td><td>27–30</td><td>2–3</td><td>40–50</td><td colspan="2">0·2–0·5</td></tr>
<tr><td>Sheep</td><td>23–28</td><td>1–2</td><td>40–50</td><td colspan="2">0·6</td></tr>
<tr><td>Bear (sloth)</td><td>29</td><td>11</td><td>52</td><td colspan="2">2</td></tr>
<tr><td>Lion</td><td>29</td><td>2</td><td>40</td><td colspan="2">3</td></tr>
<tr><td>Baboon</td><td>19</td><td>4</td><td>67</td><td colspan="2">0·5</td></tr>
<tr><td>Human</td><td>24–25</td><td>5–7</td><td>53–57</td><td colspan="2">2–2·5</td></tr>
</table>

component fatty acids) in the depot fats of the land animals belong to the C_{18} series. In many cases, apparently (detailed analyses are, curiously, still somewhat scanty in this group except for a few common animals), these acids are largely unsaturated (oleic, sometimes with polyethenoid acids) ; but in ruminant animals, at all events, stearic acid occurs in the mixed glycerides, often to a marked degree, in place of oleic acid ; and specific characteristics in the constitution of the mixed triglycerides in these depot fats, which place them apart from most other natural fats, suggest that the stearic compounds result from hydrogenation of oleic derivatives (*cf.* below, p. 21).

In the depot fats of the land animals there occurs frequently (usually in not very large amounts) the linoleic acid, $C_{18}H_{32}O_2$, which is a component of many seed fats ; but there is much reason for thinking that this is derived by assimilation from the latter. At this point it should, perhaps, also be said that the data quoted above refer to animals which have received their natural diet ; it is well known, of course, that higher animals, at all events, are able to ingest fats from vegetable seeds, etc., and to lay down some of the specific acids of the latter in their depot fats, but this aspect of fat deposition has been excluded, so far as possible, in the observations on which this survey is based.

Component acids of mammalian milk fats. These have been studied in detail in the cases of comparatively few species. The component acids of whale milk fat are almost quantitatively the same as those of its depot fat (blubber), and there is reason to believe that the same holds good for the milk fats of other marine mammalia and perhaps even for some of the more primitive forms of amphibia and land animals. In the higher land animals the C_{18} acids usually form less of the total acids than in the corresponding depot fats, the differences being approximately balanced by the appearance of lower saturated fatty acids (C_{12}, C_{10}, C_8, C_6 and C_4). Probably in many animals this phenomenon does not proceed as far as the production of butyric, hexanoic and octanoic glycerides (at all events to any marked extent), but amongst the ruminant animals it is especially in evidence. Thus cow milk fat contains about 10 mols. per cent. of butyric acid and subsidiary amounts of C_6, C_8, C_{10} and C_{12} acids ; sheep and goat milk fats contain less butyric and hexanoic acids, but more octanoic and about 10 mols. per cent. of decanoic acid. Similar differences to those which set the glyceride structure of the corresponding depot fats apart from that of all other natural fats are apparent in the component glycerides of cow and similar milk fats (*cf.* below, p. 21).

The parallelisms to be observed between fat types and evolution in the animal world, as outlined above, are clearly apparent and remarkable. It remains now to consider the corresponding sequence in the vegetable kingdom.

Component acids of vegetable fats. In the land flora, as in the fauna, the data are most abundant for depot (seed) fats of the more developed land plants ; there is at present a great lack of detailed information on the characteristic fats of the lower forms of land flora and also on the glycerides present in the growing parts of the larger plants. Nevertheless, it is interesting that the unsaturated hexadecenoic (C_{16}) acid, so characteristic of aquatic and lower land animal life, has been observed in quantity in the fats of a bacillus (diphtheria), of yeast (*Saccharomyces cerevisiæ*), and of the spores of a cryptogam (*Lycopodium*) ; whilst recently it has been shown that hexadecenoic acid is present in very small proportions (not exceeding 1 per cent.) in several of the more common seed and fruit-coat fats (groundnut, cottonseed, soya bean, teaseed oils, and olive and palm oils). There is some evidence that higher aquatic plants, including sub-aquatic grasses, have fat closely resembling that of fresh-water algæ, whilst the glycerides of forage grasses contain unsaturated C_{18} acids which are seemingly not identical with those typical of most seed fats.

The component acids of the glycerides of seeds (and, when present, of the pericarp or other fruit coat) of members of many plant families have, on the other hand, been widely studied in detail in recent years. The first thing which is apparent, in contrast to fats of aquatic flora, is considerable simplification in the component fatty acids. As in the land animals, palmitic and oleic become the most consistently prominent features ; but a third acid, linoleic, must be added to these as a component which is of most frequent occurrence. The latter acid is either absent, or only present in small quantities, in most fats of aquatic origin, but it, and the related still more unsaturated, linolenic acid, are amongst the most familiar constituents of the widely distributed class of " drying " seed oils.

Fruit-coat fats so far examined include (with at present only one or two exceptions) palmitic and oleic acids as sole major components, irrespective of the plant family in which they occur ; linoleic acid is also frequently present, but usually only in minor quantities. In many *seed fats*, also, the bulk of the component acids is palmitic, oleic, and linoleic in varying proportions ; and, in general, seed fats of the same family have a certain resemblance in the relative proportions of these component acids. Malvaceæ and Bombacaceæ seed fats, for example, are usually high in their content of palmitic acid (20–25 per cent.) and also contain about 50 per cent. of linoleic acid. The latter acid is prominent in many seed fats of the conifers, of the larger dicotyledonous trees and shrubs, and in Rosaceæ, Compositæ, Labiatæ, Linaceæ, and other families, and also in those of Gramineæ, the component acids of most of which include about 10–15 per cent. of palmitic, 30–60 per cent. of oleic, and 60–30 per cent. of linoleic.

Land plants differ, however, from all other natural sources of fats in that, in many other families, their seed fats include as major components a fatty acid (or acids) different from any of those previously mentioned; in such cases the occurrence of the specific acid is almost wholly confined to one, or at the most to only a few, of the natural plant families. Thus the unsaturated erucic acid, $C_{22}H_{42}O_2$, is present in quantity in all Cruciferous seed fats; a structural isomeride of oleic acid, petroselinic acid, is similarly found in seeds of the Umbelliferæ and the closely related ivy; and the cyclic unsaturated chaulmoogric and hydnocarpic acids in many of the Flacourtiaceæ. Of saturated acids, arachidic (C_{20}) and lignoceric (C_{24}), which occur in minute amounts in many seed fats, only attain major proportions in members of the Sapindaceæ and some of the Leguminosæ, whilst stearic acid is present in quantity only in the seed fats of a few tropical families. Saturated acids of lower molecular weight (lauric, C_{12}; myristic, C_{14}) are similarly characteristic of other, mainly tropical, families; the composition of all Palmæ seed fats yet studied is remarkable for close quantitative similarity, with lauric (45–48 per cent.) and myristic (16–20 per cent.) as main component acids.

In a few cases, as in *Ricinus communis*, *Picramnia* sp., or *Aleurites montana* and *Fordii*, the seed fats of one or two species of a genus elaborate quite distinct fatty acids—in the cases mentioned, respectively, ricinoleic (hydroxyoleic), tariric (acetylenic), and elæostearic (conjugated triethenoid). The last-named is at present exceptional in that it is quite an unusual plant fatty acid, and has yet been observed (in each case in isolated species only) in the three distinct families Euphorbiaceæ, Rosaceæ, and Cucurbitaceæ.

Although the biosynthesis of these specific fatty components places many of the higher land plant families apart from the rest of nature as regards their fat types, we are left with the circumstance that the occurrence of these unusual features runs on the whole remarkably parallel with the groups into which morphologists have placed them. Apart from the widespread occurrence of specific component acids in certain plant families, there is observed a (probably gradual) simplification in fatty acid composition, commencing from the aquatic flora and proceeding in the direction of the fruit fats of the more highly developed land plants, similar to that which may be traced in the animal world.

Ivanow[3] and others have pointed to climatic temperature as the factor mainly operative in determining the relative saturation of seed fats. Production, in plants of cooler latitudes, of fats solid at the prevailing temperatures of the atmosphere is in any case not very probable; but this is not evidence that the tropical temperature *per se* causes or favours development of the more saturated fats. Actually, many of the most unsaturated fats (those of *Aleurites*, *Hevea*, *Perilla*, *Licania* species, to quote only a few) are synthesised in the fruits of plants which can only live in tropical or subtropical conditions. On the other hand, in those plants which thrive in either hot or cold climates, the investigators quoted have demonstrated a greater production of the characteristic unsaturated acids in seeds from plants grown in the cooler regions.

THE COMPONENT GLYCERIDES OF NATURAL FATS

The very striking and characteristic differences in the fatty acid mixtures combined as triglycerides in fats from different regions of the vegetable and animal kingdoms are not reflected in the manner in which the triglycerides themselves are put together ; for, with apparently few exceptions (to which reference is made later), the fatty acids seem to be woven into molecules of triglycerides on the same simple general principle, whatever their place of origin may be—vegetable or animal, "depot" (reserve) or "tissue" (organ) fat—and whatever may be the particular mixture of acids present as component fatty acids. This simple principle (which has already been mentioned) is that nature strongly favours the elaboration of "mixed," and not simple, triglycerides. **Natural fats should be defined, in fact, as mixtures of mixed triglycerides.*** Consequently any individual triglyceride molecule tends towards maximum heterogeneity in its composition ; but, simultaneously if paradoxically, this may lead in some cases towards closer homogeneity, or fundamental similarity, in the triglycerides considered as a whole.

This will be seen if we consider a hypothetical case of a fat containing three different acids, A, B, C, combined in equimolecular proportions with the trihydric glyceryl radical C_3H_5 ⫶ (which may be written as G). The following combinations of three glycerol and nine fatty acid molecules are possible :

$$\begin{array}{llll}
\text{(i)} & G(A_3) & G(B_3) & G(C_3) \\
\text{(ii)} & \left\{\begin{array}{l} G(A_2B) \\ G(A_2C) \end{array}\right. & \left\{\begin{array}{l} G(B_2C) \\ G(B_2A) \end{array}\right. & \left\{\begin{array}{l} G(C_2A) \\ G(C_2B) \end{array}\right. \\
\text{(iii)} & G(ABC) & G(ABC) & G(ABC)
\end{array}$$

Thus the exclusive presence of simple triglycerides $G(A_3)$, etc., would, of course, result in a fat which was a mixture of three compounds, while that produced by the exclusive occurrence of triglycerides each containing only two different acids might lead to a still more heterogeneous mixture of six components. On the other hand, complete formation of the heterogeneous triglyceride molecule G(ABC) might result in the production of a single individual compound.

If we take another hypothetical case in which a fat contains only two fatty acids, with one of the latter (Y) in much greater amount than the other (y), the possibilities are as follows :

$$\begin{array}{lll}
\text{(i)} & G(Y_3) & G(y_3) \\
\text{(ii)} & G(Y_2y) & G(y_2Y)
\end{array}$$

If, in natural fats, the component fatty acids were strictly distributed, according to their relative proportions, as evenly or widely as possible amongst all the glycerol or glyceride molecules, the presence of an equimolecular mixture of *three* acids would result in the corresponding fat being an individual compound G(ABC), whilst in the other imaginary example we have considered (with only *two* fatty acids) we should expect the corresponding fat to contain a very large proportion of the mixed triglyceride $G(Y_2y)$.

This is, in fact, the main principle which seems to be operative in the structure of natural fats. Since the number of even the major component acids in a fat often exceeds three, and their relative proportions vary widely, as we have seen, in different cases, it is not often that we encounter instances which approach in simplicity the hypothetical combinations which have just been discussed. Furthermore, fats, as products of a series of complex changes in a living organism, need not be expected to conform rigidly—and indeed rarely do so—to the exact demands of a numerical formula. Thus, where it has been possible to study seed fats containing, for example, twice or more than twice as much saturated as unsaturated acids, it is found that the triglycerides which contain saturated and unsaturated acyl groups are not wholly made up of disaturated-mono-unsaturated glycerides $G(S_2U)$, but contain a mixture of about 75–80 per cent. of this form with 25–20 per cent. of monosaturated-di-unsaturated glycerides $G(SU_2)$. Any excess of saturated acids above the mean ratio demanded by this mixture (or " association ratio," as it has been called,[4] of about 1·4–1·5 mols. of saturated per mol. of unsaturated acid) appears as fully saturated triglycerides, $G(S_3)$.

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* As first suggested, apparently, by F. Guth (1902).

It is important to be explicit as to the meaning of the term " even distribution " as it has come to be applied in connection with the glycerides in natural fats. It can perhaps best be defined in the following manner :

(i) When a given fatty acid A forms about 35 per cent. (mol.) or more of the total fatty acids $(A+X)$ in a fat, it will occur at least once, $G(AX_2)$, in practically all the triglyceride molecules of the fat in question.

(ii) If it forms from about 35 to about 65 per cent. (mol.) of the total fatty acids $(A+X)$, it will occur twice, $G(A_2X)$, in any given triglyceride molecule in some instances, and of course more frequently the higher the proportion of this acid in the total fatty acids.

(iii) If it forms 70 per cent. or more of the total fatty acids, the remaining fatty acids (X) can at most only form mixed glycerides $G(A_2X)$, and the excess of A then, and broadly speaking then only, appears as a simple triglyceride, $G(A_3)$.

(iv) A minor component acid which forms much less than about a third of the total fatty acids (e.g. 15 per cent. or less), will not occur more than once in any triglyceride molecule (and, of course, not at all in many of the triglyceride molecules).

The above statement covers broadly the mode in which " even distribution " of fatty acids in glyceride molecules operates in the natural fats. In the majority of cases the effect is quite other than that which would result if the fatty acid molecules were distributed on an indiscriminate or random basis. In the case of completely random distribution, the amount of a simple triglyceride $G(A_3)$ which should be present in a fat is calculable and proportional to the cube of the percentage of the fatty acid A in the total fatty acids of the fat. Thus, if A formed half of the fatty acids, the percentage of $G(A_3)$ in the fat would be 12·5 ; with 65 per cent. of A in the total acids, the percentage of $G(A_3)$ would be 27·5, on the basis of completely random distribution.

It has been pointed out that the general tendency to produce, as it were, as little of simple triglycerides (containing three radicals of the same fatty acid) as possible, and to concentrate on the production of molecules of mixed triglycerides, is extremely marked throughout the whole range of natural fats. Within this broad and, on the whole, accurate generalisation, there are, however, a few exceptions or, rather, modifications to be considered ; these instances are nevertheless by no means modifications in the sense of presenting a greater proportion of simple triglycerides, but rather the reverse—extensions, as it were, of the principle of heterogeneity of molecular triglyceride structure. To describe the evidence on which the above statements are based involves the detailed consideration of many specific cases, and their complete explanation must, therefore, be deferred until the component glycerides of the different classes of natural fats are being fully discussed in Chapters VI and VII. It is desired at this stage, however, to offer a rapid survey of the subject analogous to that attempted in the preceding pages on the component acids of the fats.

It is fair to preface such a survey by a word on the differences in the experimental technique necessary for handling each aspect of the subject. The determination of component acids in a fat, although somewhat complicated and lengthy, is usually a matter of reasonable accuracy and precision. The state of affairs as regards the component glycerides of a fat is very different. Except in a few special cases, physical methods of separation are incapable of giving more than, at best, a very partial separation of the natural mixture of mixed triglycerides into a series of somewhat simpler mixtures. Chemical methods of attacking the problem must therefore be sought, and these are restricted by the nature of the compounds to be studied (including, in particular, the necessity for avoiding any undesired hydrolysis of the glycerides in the course of any of the processes used). The experimental attack is, as a matter of fact, frequently indirect in nature. These and similar conditions combine to make the investigation of glyceride structure, especially on a quantitative basis, a much more involved and tedious business than that of the component acids alone. It may be added that quantitative study of component glycerides in natural fats has only been undertaken since about 1927.

Component glycerides of marine animal fats. The large number of component acids in these fats, and their highly unsaturated nature, causes the mixture of component glycerides to be very complex and their study to be almost beyond the reach of the methods available. Nevertheless a few members of this group, notably whale oil, cod liver oil and a few other fish oils, have been investigated by converting the mixed glycerides into bromo-additive products,* many of which are crystalline at room temperatures or somewhat lower; the brominated glycerides have been separated by fractional crystallisation from appropriate solvents and in a number of cases individual mixed brominated glycerides have been identified. The results suggest that, in this group of fats, most of the triglyceride molecules contain at least two, and frequently three, different acids in combination. Study of the fully saturated glycerides produced at various stages of catalytic hydrogenation ("progressive hydrogenation" †) of whale oil and cod liver oil has also given results which point clearly to the presence of many mixed glycerides in these fats. More recently, the glycerides of whale and of herring oils have been partly segregated into somewhat simpler groups by systematic crystallisation from acetone ‡ at temperatures between 0° and −40°; the chief types of glyceride in each fraction isolated can then be deduced to a certain extent from the component fatty acids determined by ester fractionation in each of the fractions.

Even the unusual *iso*valeric acid of the depot fats of the dolphin and porpoise has been shown [5] to be present therein not to any notable extent as "tri-*iso*valerin" but almost wholly in the form of mixed triglycerides in which one or two acyl radicals are those of the typical higher fatty acids of the marine oils.

So far as experimental evidence goes at present, therefore, it is wholly in favour of the view that the triglyceride molecules of marine animal fats are extremely heterogeneous in character. The marine animal fats appear to be consistent and pronounced instances of the "rule of even distribution"; the fatty acids are distributed evenly amongst the triglyceride molecules, so that (because of the large number of different fatty acids present) very many of these contain three different acyl groups

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* See Chapter V, p. 228.
† See Chapter VII, pp. 289–291.
‡ See Chapter VII, pp. 291–293.

Component glycerides of land animal fats. It has been mentioned that the fats of higher land animals have been observed to contain considerable and approximately constant proportions of palmitic acid (25–30 per cent.). Nevertheless, so long as only minor proportions of other saturated acids are present, only very small proportions (2–3 per cent.) of fully saturated glycerides have been detected in these fats. The determination of the amount of fully saturated glycerides * (i.e. triglycerides in which all three acyl groups are those of saturated fatty acids) can be effected fairly easily by the method first described by Hilditch and Lea,[6] whereby all unsaturated glycerides are converted (by oxidation in acetone solution with finely powdered potassium permanganate) into acidic glycerides and only the fully saturated components remain eventually as neutral compounds. The absence of any appreciable amount of fully saturated glycerides (e.g. tripalmitin) from animal depot fats in which 30 per cent. of palmitic acid is included shows that the latter is present almost wholly in the form of mixed palmito-unsaturated triglycerides and, thus far, that the usual tendency towards maximum mixed-glyceride formation is in evidence.

In the depot fats of the pig, ox, sheep, and some other herbivorous animals, in which stearic acid attains more important proportions (in addition to the usual 25–30 per cent. of palmitic acid) the proportion of fully saturated glycerides becomes considerable even when the total amount of saturated acids is still below 60 per cent. of the total fatty acids present. The same feature is observed in the milk fats of this group of animals and, although it does not connote any closer approach to a simpler type of glyceride structure, it indicates an important general characteristic in the component glycerides of these fats. They are therefore considered as somewhat outside the customary series of natural glycerides and are grouped below with other departures from what appears to be the general "rule of even distribution."

Component glycerides of vegetable fats. Seed fats and fruit-coat fats have been more fully studied with reference to their glyceride structure than any others except pig, ox, and sheep depot fats, mainly because the comparative simplicity of the mixtures of component acids present in many cases causes the fats in question to lend themselves more readily to the chemical methods of investigation of the glycerides. Much information has been obtained by determination of the fully saturated glycerides present *; in addition two other procedures have been at times employed, namely, examination of the fully saturated and mixed saturated-unsaturated glycerides present in a series of fats which have been progressively hydrogenated to different extents,† and determination of the tristearin content of a completely hydrogenated fat ‡ (this, of course, gives the approximate amount of all the triglycerides made up only of C_{18} acids (whether stearic, oleic, linoleic, or linolenic) which are present in the original fat).

* See Chapters VI, pp. 232–236; XI, pp. 513–516.

† See Chapter VI, pp. 238–241.

‡ See Chapters VI, p. 239; XI, pp. 517–519.

The most recent advance in the study of glyceride structure of natural fats consists in effecting a partial resolution into several fractions by systematic and quantitative crystallisation from acetone, either at temperatures from 20° down to 0° or —10° (for fats solid at the ordinary temperature), or from 0° to as low as —60° (for liquid fats).* Each fraction is then studied in detail, first by determination of its component acids, then (where necessary) by detection of fully saturated glycerides (and their component acids), or by the hydrogenation procedures just mentioned. In this way, in most land vegetable and animal fats, it is possible to obtain (*a*) fractions in which fully-saturated and mono-unsaturated glycerides predominate, with a little di-unsaturated material; (*b*) fractions containing almost wholly mono-unsaturated mixed with di-unsaturated glycerides; and (*c*) fractions containing almost exclusively di-unsaturated and tri-unsaturated glycerides. It has thus become possible, in many of the fats which contain only two, three or four major component acids, to give the approximate amount of each of the major component glycerides present.

Fruit-coat fats. Palm and olive oils, and Chinese (*Stillingia*) vegetable tallow are familiar examples of this class. The component glycerides of fruit-coat fats seem for the most part to be of the " evenly distributed " type. Thus palm oils contain almost 90 per cent. of mixed dipalmito-" oleins " † and palmitodi-" oleins," whilst olive oil (the mixed fatty acids of which include about 75 per cent. oleic and 8 per cent. linoleic acid) contains not much more than 60 per cent. of oleo-linoleic glycerides and probably less than 50 per cent. of triolein. The simple triglyceride, tripalmitin, however, is frequently present in fruit-coat fats: in palm oil this may amount to 7-10 per cent. of the whole fat whilst olive oil (with only 10 per cent. of palmitic acid) may contain 2 per cent. of tripalmitin. On the other hand it is almost, if not wholly, absent from other fruit-coat fats, such as " piqui-a," which, like palm oils, contain 35–45 per cent. of palmitic in their mixed fatty acids.

Seed fats. However varied the fatty acids in seed fats may be, the resulting triglycerides are, almost without exception, fundamentally similar in type. No simple triglyceride appears unless one acid is so much in excess of the others that this necessarily happens. Thus, if the amount of triglycerides wholly made up of saturated acids is compared with the proportion of saturated acids in the total fatty acids, it has been found that fully saturated glycerides do not appear in quantity until saturated acids form more than 60 per cent. of the whole. In the latter case the amount of fully saturated glycerides present is approximately that left over after the maximum amount of mixed glycerides has been laid down so as to contain relative proportions of about 60 of saturated to 40 of unsaturated acids. [It will be noticed that, to use the terminology on p. 15, a mixture of about 3–4 mols. of " $G(Y_2y)$ " with one of " $G(Yy_2)$ " appears to be the rule, rather than exclusive production of " $G(Y_2y)$."]

The solid seed fats have given much detailed information on glyceride structure, because in many cases there is sufficient of fully saturated glycerides for the component acids of the latter to be determined by the ester-fractionation procedure. Moreover, in certain instances where the fats are composed substantially of only oleic with two saturated (e.g. palmitic and stearic) acids, considerable proportions of mono-oleo-disaturated glycerides are present; these give rise during permanganate-acetone oxidation to the corresponding mono-azelao-glycerides, which can sometimes be utilised for further characterisation of the mono-oleo-glycerides [*] (the azelao-saturated glycerides are, however, unfortunately very prone to hydrolysis, and are also very difficult to obtain free from admixed nonanoic acid—another by-product of the oxidation; their utility is hence somewhat limited). The mono-oleo-disaturated glycerides of certain seed fats seem to give rise to β-azelao-disaturated glycerides, which implies that the former occur as β-oleo-glycerides only; β-oleo-$\alpha\alpha'$-distearin, for example, in *Allanblackia* and *Palaquium* fats. Similarly, in liquid seed fats (e.g. cottonseed oil) in which palmitic forms less than 30 per cent. of the total acids and is practically the only saturated acid present, β-palmitodistearin has been observed to be the only form of palmitodistearin produced by catalytic hydrogenation.

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* See Chapters VI, pp. 241–244, 276, 284; XI, pp. 520–526.

† For convenience, where, as often happens, the unsaturated acids consist of 80–90 per cent. of oleic with 10–20 per cent. of linoleic acid, they are referred to together as " oleic " acid or, as glycerides, " oleins." The absence of inverted commas denotes that oleic acid as an individual compound is to be understood.

The selective production of one isomeric form of a triglyceride (which appears, incidentally, to hold, at least in some cases, in animal as well as in vegetable fats) is rather striking, especially in its contrast to the mixed character of the natural glycerides as a whole. Apparently the fatty acids are interwoven with the glycerol molecules so as to avoid, where possible, approach to triglycerides containing identical acyl radicals but, concurrently, the mixed glycerides are not produced indiscriminately, but are given preferred configurations. From the evidence available (much too slender at present to be conclusive) it might be conceived that the acid present in lesser quantity may take up the β- or central position in the glycerol molecule.[†]

The similar study of liquid vegetable fats, such as cottonseed, olive or linseed oils, requires other methods in addition to the determination of fully saturated glycerides (which in these cases usually merely demonstrates their absence). The content of glycerides wholly made up from C_{18} acids can, however, be ascertained by two procedures, namely, study of the glyceride structure of the oil after progressive hydrogenation to varying degrees,[‡] and estimation of the tristearin content of the completely hydrogenated fat.[§] In all cases so far studied, the results obtained by the application of either method indicate that the quantity of tri-C_{18} glycerides present in each fat is near to the minimum possible (which may be calculated from the composition of the mixed fatty acids of the oil). This proves that the usual "rule of even distribution," i.e. the avoidance as far as possible of simplicity in individual triglyceride molecules, is followed in the liquid seed fats which have been examined, just as it holds for the solid seed fats; in other words, that the glyceride structure is independent of whether, in the acids concerned, saturated or unsaturated acids predominate. It is also in harmony with qualitative observations on the separation of various components of some liquid seed fats in the form of bromo-additive products, and with the evidence obtained in more recent investigations of some liquid vegetable fats (*e.g.*, olive, cottonseed, and niger seed oils) from the component acids found in fractions of the fats isolated by crystallisation from acetone at low temperatures (*cf.* above, p. 19).

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[*] See Chapters VI, pp. 262, 265; XI, pp. 514, 515.

[†] See Chapter VI, pp. 271, 272.

[‡] See Chapter VI, pp. 238–241.

[§] See Chapters VI, p. 239; XI, pp. 517–519.

Digressions from the usual "evenly distributed" type of glyceride structure. The only instances in which any notable divergence has been observed from the principles of glyceride structure described in the preceding pages are enumerated below :

1. *Depot and milk fats of ruminants* (*ox, sheep, buffalo, etc.*). It has already been mentioned that in the depot fats of this group, in which stearic acid is an important component, the structure of the mixed glycerides is also distinctive : the amount of fully saturated glycerides (mixed palmitostearins in these cases) is much greater, for a given ratio of saturated to unsaturated acids in the whole fat, than in "evenly distributed" seed fats of corresponding composition. For example, we have seen that seed fats, whose mixed fatty acids contain 60 per cent. of saturated acids, still contain almost negligible quantities of fully saturated glycerides ; but a tallow of similar general composition (i.e. with about 30 per cent. of palmitic and 25 per cent. of stearic acid in the mixed acids) contains about 26 per cent. of palmitostearins. In the other direction, pig back fats may contain as little as 7 per cent. of stearic acid with the usual 25 per cent. of palmitic acid (thus far resembling rat or bird fats); in such cases the amount of fully saturated glycerides is very small (about 2–5 per cent.) and the fat conforms more nearly to the usual "evenly distributed" type. Between these extremes, tallows and lards contain stearic and oleic acids in proportions which vary more or less inversely, the sum of the two being fairly constant in any one specimen of depot fat ; and the greater the amount of stearic acid (with correspondingly less oleic acid) the greater is the proportion of fully saturated glycerides.

The corresponding milk fats (the component acids of which, in addition to about 25 per cent. of palmitic and somewhat varying amounts (35–45 per cent.) of oleic acid, include important proportions of butyric and other saturated acids of low molecular weight as well as some stearic and myristic acids) are exactly similar to the depot fats in their unusually high proportions of fully saturated glycerides. Indeed, when the content of fully saturated glycerides is plotted graphically against the total amount of saturated acids in the mixed fatty acids, the whole series, for both depot and milk fats, lies on a smooth curve.

The increase of stearic at the expense of oleic acid in the more saturated depot fats is in conformity with saturation or hydrogenation of an initially more unsaturated fatty acid mixture ; the parallel increase in fully saturated glyceride contents suggests that it is preformed oleic *glycerides*, not acids, which are undergoing hydrogenation. In the milk fats it has been suggested that, similarly, the lower saturated fatty acids may be produced in the mammary gland, by simultaneous oxidation and reduction processes, from preformed oleic (or, possibly, octadecadienoic) *glycerides*. For further discussion of these points, however, the reader must be referred to later chapters (III, pp. 90, 91, 96, 117 ; VII, pp. 306–309).

2. *Vegetable fats.* (a) *Fruit-coat fats.* It has been pointed out (p. 19) that some fruit-coat fats contain definitely more tripalmitin than would be

expected according to the usual operation of the " rule of even distribution." This was first noticed in the cases of palm oils and olive oils, and put forward as a fairly well-marked exception to the rule, although admittedly the actual proportions of fully saturated glycerides were not, in the nature of the case, very large. Later studies of other, less common fruit-coat fats have uniformly shown the latter to be built up wholly on the principle of " even distribution." It appears uncertain at the moment, therefore, whether it is more accurate to say that " some fruit-coat fats are somewhat anomalous in glyceride structure," or that " all fruit-coat fats, with the exception of palm oil and olive oil, closely follow the rule of even distribution."

(b) *Seed fats.* Out of the numerous examples which have now been examined, only two seed fats, those of *Laurus nobilis* (laurel oil) and *Myristica malabarica* show pronounced divergence from the usual " evenly distributed " structure. No apparent explanation is available to account for these two cases which curiously (like palm and olive oils in the fruit-coat fats) were encountered in the earliest days of quantitative study of glyceride structure. The fat of *Myristica malabarica,* however, is also notable for containing considerable amounts of resin acid, apparently combined as glyceride.

This is not to say, of course, that maximum even distribution is to be observed in any particular seed fat. The group of solid seed fats which have about 60 per cent. of saturated acids in the total acids, and of which cacao butter is a familiar example, usually contain very minor amounts (frequently about 2 per cent.) of fully saturated components. Small variations of this order do not, of course, affect the validity of a generalisation applying to a widely diverse group of natural products. Similarly, but less frequently, in the same class of fats, the presence of a very small amount of triolein has been detected (incidentally, it may be remarked, the detection of a small proportion of triolein is much more difficult than that of the same proportion of fully saturated glycerides). It may be significant, however, that the simple triglyceride triolein has been less often detected in these cases than the fully saturated components, which are almost invariably, in this group, mixed palmitostearins.

It is hoped that this somewhat lengthy introduction will serve to outline the method of treatment to be adopted in the following chapters, and to indicate the chief aspects of the field which are treated in the latter in fuller detail.

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CHAPTER II

THE COMPONENT ACIDS OF FATS OF AQUATIC FLORA AND FAUNA

It was pointed out in the previous chapter that the general analytical characteristics of fats are usually insufficient to define their specific composition—detailed data for at least the major component acids are required for this purpose. Attention must, therefore, be concentrated upon the results of comparatively recent analyses made by means of the fractional distillation of esters of fatty acids which have been given a preliminary separation, e.g. by taking advantage of the differing solubilities of their lead (or lithium) salts in appropriate organic solvents.* Such analyses, although now fairly numerous, cover only a small fraction of the natural fats of which the average analytical characteristics have been determined, and, of course, a still smaller proportion of the fats which exist in all the diverse organisms of plant and animal life. The detailed data, on which we must depend for the present purpose, therefore represent at the moment, as it were, a very rough sampling of the total material—a sampling which, moreover, is very uneven, the data being much more abundant, for example, for seed fats than for fats of aquatic flora, and so on. A cautionary word is thus advisable, to warn the reader that the subject, as about to be described, is in a state of very active development. The broad outlines have been defined, and in many groups details of specific differences have been filled in equally definitely; but, in other groups which have so far received less thorough investigation, we may anticipate that further research will lead to fresh developments and, it may well be, some modification of the descriptions and classifications given in this and the next few chapters.

The general analytical characteristics of an exceedingly large number of fish oils have been recorded, and in nearly all cases it has been found that the mixed fatty acids yield fairly large proportions of ether-insoluble octa- and deca-bromo addition products (usually amounting to 30–50 per cent. of the total weight of the mixed fatty acids). In most cases, also, the percentage of saturated acids has been determined by the lead salt method, and in a number of instances (more especially in the hands of Japanese workers) the proportion of highly unsaturated acids with acetone-soluble lithium salts has also been given. Such data are at best, however, only partial when dealing with the complex mixture of component acids characteristic of marine animal fats.

The ester-fractionation method of analysis leads to figures for the percentages of each saturated acid and of each group of unsaturated acids of the same carbon content, with a value for the mean state of unsaturation of the latter. The mean unsaturation is conveniently expressed by the number of hydrogen atoms necessary to restore a molecule of the acid to the saturated state: thus (—4·0H) indicates an average unsaturation corresponding with two double bonds, but does not necessarily imply only the presence of a diethylenic acid.

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* See Chapter XI, pp. 468–471.

In the complex mixtures of acids encountered in fats from aquatic sources, the order of accuracy of the ester-fractionation analyses is probably less than in those of simpler fatty acid mixtures, but the divergence from the truth is unlikely to exceed 2 or 3 units per cent. in extreme cases. This degree of uncertainty does not have a serious effect for the present purpose, because the type differences which are discernible may involve differences of 5–10 units per cent., or even more, in the proportions of one or other of the component acids.

So far as it is possible to determine at present, it would appear from the general characteristics already referred to that most fats of aquatic origin possess compositions of the same type as those of their respective classes for which detailed fractionation data are available. The detailed analyses, at the same time, demonstrate clearly that different groups of aquatic organisms display certain subordinate type differences in the proportions of the various major component acids. It is curious, nevertheless, that in very many cases throughout the whole series of marine animal oils the total proportion of saturated acids is relatively constant and in the neighbourhood of about 20 per cent., whilst, similarly, palmitic acid most frequently forms from 12 to 15 per cent. or thereabouts of the mixed fatty acids.

Fats from the various forms of aquatic life will now be discussed, commencing with those of vegetable and lower animal organisms.

COMPONENT ACIDS OF FATS OF AQUATIC FLORA AND MICRO-FAUNA

The presence of the characteristic highly unsaturated C_{20-22} acids of fish fats in a large number of algæ was observed in 1925 by Tsujimoto,[1] who isolated them in the form of ether-insoluble polybromo-additive products, but noticed that the yield of the latter was much less than in the case of the majority of fish liver oil acids. Later, Collin [2] made partial analyses of small quantities of fats from plankton collected by Dr. E. R. Gunther and Prof. J. C. Drummond, with the following approximate results:

	ZOOPLANKTON FAT (Per Cent.)	PHYTOPLANKTON FAT (Per Cent.)
Saturated acids	17·3	15·5
Highly unsaturated acids (from ether-insoluble polybromides)	9·6	2·1
Highly unsaturated acids (from acetone-soluble lithium salts)	43·6 (iod. val. 311)	—

Detailed analyses of fats from several species of algæ, both marine and fresh-water, were given by Lovern [3] in 1936 (Table 1, p. 25).

We shall shortly see that the fats of aquatic animals, large and small, differ typically in their proportions of certain component acids according to whether the habitat of the animal is salt- or fresh-water. From the information so far available in Table 1, however, it seems that this distinction does not hold in the case of aquatic plants. Lovern (*loc. cit.*) makes the following comments on his results:

TABLE 1. *COMPONENT ACIDS (WTS. PER CENT.) OF FATS OF ALGÆ, ETC.*

		SATURATED				UNSATURATED				
CLASS	SPECIES	$C_{<14}$	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Chlorophyceæ	*Nitella opaca* *	—	6	18	3	3 (>−2·0H)	34 (−2·5H)	23 (−4·5H)	13 (−5·8H)	—
	Oedogonium sp.*	—	2	20	1	—	32 (−3·1H)	35 (−4·6H)	9 (−?H)	1 (−?H)
	Cladophora sauteri *	Trace	12	10	2	Trace	19 (−4·7H)	49 (−3·8H)	8 (−7·1H)	—
	Mixed †	—	4	10	2	3 (>−2·0H)	39 (−3·4H)	30 (−5·1H)	8 (−6·5H)	4 (−?H)
Phæophyceæ	*Fucus vesiculosus* (1) †	Trace	8	9	1	Trace	6 (−2·0H)	57 (−3·2H)	16 (−7·3H)	3 (−?H)
	Fucus vesiculosus (2) †	Trace	9	7	2	1	5 (−2·0H)	63 (−3·0H)	13 (−7·3H)	—
	Laminaria digitata †	—	6	14	1	2	11 (−2·0H)	42 (−4·2H)	24 (−8·1H)	—
Rhodophyceæ	*Rhodymenia palmata* †	1	4	19	1	Trace	6 (−2·9H)	20 (−4·5H)	36 (−9·2H)	13 (−?H)
Higher plant	*Anacharis alsinastrum* *	1	1	15	5	2	25 (−3·0H)	39 (−4·9H)	12 (−6·0H)	—
Diatom	*Nitzschia closterium* †	—	8	17	2	1	36 (−3·4H)	20 (−5·3H)	16 (−7·0H)	—

* Fresh-water species. † Marine species.

"In the algæ the properties seem to follow the colour grouping. Of the green algæ three were fresh-water species and one marine.

"The saturated acid percentages show great irregularities throughout, but for the unsaturated acids some interesting correlations occur. For the green algæ (Chlorophyceæ) the predominating unsaturated acids are those of 16 and 18 carbon atoms, with little C_{20} and little or no C_{22} acids. The degrees of average unsaturation of the C_{16} and C_{18} acids are unusually high. In the brown algæ (Phæophyceæ), C_{16} unsaturated acids have not the same importance, C_{18} acids are outstanding, and C_{20} acids are present in somewhat greater proportions than for most green algæ. The C_{16} acid is mono-ethylenic only, and the C_{18} acids are not on the whole of an unusually high degree of unsaturation. For the one red alga (Rhodophyceæ) examined C_{20} acids are the major constituent and appreciable quantities of C_{22} acids are present. C_{16} unsaturated acids, whilst not present in large amounts, are again of a relatively high degree of average unsaturation.

"Turning to the higher plant *Anacharis alsinastrum*, we find a fatty acid mixture very similar to that of green algæ.

"The marine diatom *Nitzschia closterium* has a fatty acid mixture also closely resembling that of a green alga, although this diatom is brown in colour.

"Taking these fats as a whole it may be said that the fats of all the green algæ, the pondweed and the diatom are of a type very similar in many respects to fresh-water animal fats. The brown algal fats are really of a class by themselves, but more like a fresh-water than a marine animal fat. The red algal fat is the only one approximating in composition to a marine animal fat."

Further analyses by Harper [4] of the pondweed (*A. alsinastrum*) glycerides from the same source, but collected at different times, have given the following results:

DATE OF COLLECTION	November 1934 (Lovern,[3] *cf.* Table 1)	July 1935 (Harper [4])	July and October 1935 (composite) * (Harper [4])
Component acids (*weights per cent.*)			
Saturated			
C_{14}	2	2	—
C_{16}	15	21	16
C_{18}	5	2	3
C_{20}	—	—	1
Unsaturated			
C_{12}	—	3	3
C_{14}	2	6	2
C_{16}	25	20	6
C_{18}	39	39	64
C_{20}	12	7	5

* About one-third of this material was collected in July and was probably the same as that analysed under " July 1935."

It is evident that two essentially different types of fatty acid mixture have here been encountered; both belong to Lovern's general " fresh-water," and not to his " marine " type, but the specimen with a very high unsaturated C_{18} acid content (the component acids of which somewhat resemble those of the marine alga *Fucus vesiculosus*, Table 1) shows therein a transition towards the typical fats of the higher land plants.

Perhaps the most interesting feature of Table 1 is the clear indication that in the algæ fats (as in the seed fats of the higher plants) the compositions fall into groups agreeing with their botanical relationships, irrespective of their habitat (fresh-water or marine).

The component acids of the fat of the marine alga *Cystophyllum hakodatense*, Yendo, were found by Takahashi and co-workers [75] to include myristic 4·5, palmitic 18·5, unsaturated C_{16} 16(−2·0H) and 7(−8·0H), un-

TABLE 2. *COMPONENT ACIDS (WTS. PER CENT.) OF FATS OF ZOOPLANKTON CRUSTACEA (LOVERN*[9]*)*

	SATURATED				UNSATURATED				
	$C_{<14}$	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Daphnia galeata *	1	3	13	2	3 (>−2·0H)	21 (>−2·0H)	45 (−5·0H)	12 (−8·0H)	—
Diaptomus gracilis *	—	3	20	2	—	16 (>−2·0H)	34 (−4·5H)	25 (−7·1H)	—
Cyclops strenuus *	—	6	16	1	3 (>−2·7H)	30 (−3·0H)	25 (−5·2H)	16 (−8·6H)	3 (−?H)
Calanus finmarchicus †	—	8	11	1	1	12 (−2·4H)	17 (−5·1H)	25 (−7·8H)	25 (−8·1H)

* Fresh-water species.

† Marine species.

saturated C_{18} 39(−2·0H), 3(−4·0H), 1(−6·0H) and 7(−4·0H), and unsaturated C_{22} 1(−4·0H) and 3(−6·0H) per cent. (wt.).

Only a few fats of minute aquatic animal organisms have so far been examined (Table 2, p. 27), but here the typical distinction between fresh- and salt-water fats is at once seen.

So far as this evidence goes, the fresh-water micro-fauna exhibit fats with typically high contents of unsaturated C_{16} and C_{18} acids, and almost complete absence of unsaturated C_{22} acids, whereas the marine copepod fat is rich in unsaturated C_{22} acids and low in its content of unsaturated C_{16} and C_{18} acids. *D. gracilis* fat is the " least typically fresh-water fat " of the three, but even here the entire lack of C_{22} acids and the high content of unsaturated C_{18} acids would put this fat into the " fresh-water " group.

In all the fats enumerated in Tables 1 and 2, a point of interest is the extremely high average unsaturation of the C_{18} and C_{20} acids, together with the presence of polyethenoid C_{16} acids in nearly all cases. In the fats of more developed aquatic animals, almost all the unsaturated C_{16} acid is made up of hexadecenoic acid, and only very minor amounts of polyethenoid C_{16} acids are present. It is also to be noted that all the fats in question contain large amounts of " unsaponifiable matter," and that the presence of higher fatty alcohols is strongly suggested, although not definitely proved ; the latter were also noticed in the zooplankton fats examined by Collin.[2]

COMPONENT ACIDS OF FATS OF LARGER AQUATIC INVERTEBRATES

Only two component fatty analyses seem to be available at present in the case of somewhat larger invertebrates, namely, the mussel and the prawn. A detailed analysis has been given for the fat of another invertebrate, the crab *Birgus latro* ; this however is a special case (*v. infra*) since much of the fat of this crab is probably derived directly from its food.

Lovern[6] has separated the fatty matter of mussels (*Mytilus edulis*) into mainly glyceride (59–68 per cent.) and mainly phosphatide (41–32 per cent.) fractions, and records the following amounts of the usual fatty acids for each fraction :—

COMPONENT FATTY ACIDS (weights per cent.)	GLYCERIDES	PHOSPHATIDES *
Saturated		
C_{14}	2	—
C_{16}	17	27
C_{18}	2	6
Unsaturated		
C_{14}†	Trace	—
C_{16}§	11 (−2·5H)	5 (−3·2H)
C_{18}	21 (−4·1H)	17 (−4·0H)
C_{20}	30 (−7·3H)	32 (−6·0H)
C_{22}	14 (−9·3H)	13 (−8·5H)
C_{24}	3 (−?H)	?

* These acids formed about 80 per cent. of the total acidic matter recovered from the phosphatides ; of the remainder, about half were highly unsaturated acids of higher molecular weight (mean ca. C_{28}) and about half acids of a non-fatty nature, not esterified by methyl alcohol in presence of sulphuric acid.

The glyceride acids belong to the typical " marine fat " class, and resemble those of the lower marine animals (Table 2) more closely than those of the larger fish. The phosphatide acid figures are interesting because they show divergences from the glyceride acids, some, but not all, of which resemble those observed between the phosphatide and glyceride fatty acids of the liver fats of some of the larger land mammals (*cf.* Chapter III, pp. 106–110).

Klem[7] obtained figures of a somewhat similar order for the total fatty matter of the prawn (*Leander serratis*). The prawn oil, which amounted to about 1·5 per cent. of the (wet) weight of the prawns and contained 6·6 per cent. of unsaponifiable matter, contained acids of the following approximate composition : saturated series—C_{14} 1·5 per cent., C_{16} 9·5 per cent., C_{18} 2 per cent., C_{20} traces ; unsaturated series—C_{14} 0·5 per cent., C_{16} 13 per cent. (—2H), C_{18} 32 per cent. (—3·3H), C_{20} 34 per cent. (—6H) and C_{22} 7 per cent. (—10H).

Some scattered information has been recorded with reference to a few crab fats. Tsujimoto[91] found that the acids from the liver oil of a Japanese crab, *Paralithodes camtschatica*, included 85 per cent. of liquid unsaturated acids, mainly of the C_{18}, C_{20} and C_{22} series—thus belonging apparently to the general " aquatic " type.

More attention has been paid to the body fat of the land crab, *Birgus latro*, which is common in the islands of the East Indies and the Indian Ocean. Early observations[92] suggested the presence of considerable proportions of lauric acid and minor proportions of lower, steam-volatile saturated acids in the fat of this species. An analysis of the fat of land crabs from the Seychelles Islands by Hilditch and Murti[93] showed the component acids to include octanoic 1·5, decanoic 5·3, lauric 47·5, myristic 19·0, palmitic 13·1, stearic 1·7, with unsaturated C_{14} 0·7, C_{16} 2·2, C_{18} 6·8 and C_{20-22} 2·2 per cent. (mol.). These figures suggest a combination of about 75–80 per cent. of coconut oil acids with about 25–20 per cent. of more or less typical marine fat acids ; this land crab fat (*cf.* Chap. VII, p. 296) contained about 66 per cent. of fully saturated glycerides almost identical in fatty acid composition with the corresponding glycerides of coconut oil. *Birgus latro* is peculiar in that it feeds extensively on coconuts, and this circumstance almost certainly leads to much of its depot fat being derived by assimilation of coconut fat. It thus represents a special case and cannot be regarded as a typical crustacean or marine invertebrate fat in this respect.

Although the individual instances of fats from lower aquatic organisms so far studied are few in number, the relationships disclosed in their component fatty acids are of definite interest when compared with those disclosed by the corresponding and more abundant investigations which have been made of the component acids of fats from fish and marine mammalia.

COMPONENT ACIDS OF FISH FATS

The compositions of the fatty acids of many fish oils—either flesh oils or, most often, liver oils *—are now known with reasonable certainty, but even here, of course, those which have been investigated in detail are a very small fraction of the whole of the group. It was recognised many years ago, naturally, that the properties of the marine animal oils differed from those of most other then known fats, especially in their very unsaturated character and the avidity with which they absorb oxygen from the air and become partially converted into viscous and gum-like materials. A few historical notes on the recognition of some of the qualitative features of the group may be of interest before we discuss more fully the fish oil fatty acids as known at the present time.

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* It should be noted that the livers of many fish, in contrast to those of land animals, are often rich in fat and frequently serve as the main fat depot of the fish.

One of the most prominent specific component acids of marine animal oils, hexadecenoic acid, $C_{16}H_{30}O_2$, was recognised as a constituent of the head oil of the sperm whale by Hofstädter,[8] who therefore called it "physetoleic acid," as far back as 1854, and in 1898 Ljubarsky [9] noticed the same acid in seal oil. It seems to have been first recorded in a fish (as distinct from a marine mammal) in 1906 by Bull,[10] who isolated it in a fairly pure condition from cod liver oil, confirmed its formula as $C_{16}H_{30}O_2$, and converted it into a dihydroxypalmitic acid; Lewkowitsch [11] suggested the name *palmitoleic acid* by which it is usually known in Europe and America. Toyama [12] and other Japanese chemists, from about 1924 onwards, isolated the same acid from a large number of Pacific fish and whale oils under the name *zoomaric acid*; its chemical constitution having been shown in all cases to be that of Δ^9-*hexadecenoic acid*, it seems preferable, perhaps, to refer to it by its systematic name and to allow the use of the older specific names to lapse.

Of other characteristic mono-ethenoid acids of fish oils, gadoleic acid, $C_{20}H_{38}O_2$, was also discovered in cod liver oil by Bull [10] in 1906, and shown later by Toyama [13] *et al.* to be Δ^9-eicosenoic acid; the corresponding acid $C_{22}H_{42}O_2$, termed cetoleic acid by Toyama,[14] was shown by this worker to have the constitution of Δ^{11}-docosenoic acid. Tsujimoto [15] drew attention in 1927 to a Δ^{15}-tetracosenoic acid, $C_{24}H_{46}O_2$, in shark oil which he named selacholeic acid; this acid frequently occurs in the oils of Elasmobranch (cartilaginous) fish, but has not yet been detected with certainty in those of any of the Teleostid group. It is identical with the nervonic acid obtained by Klenk [16] from brain cerebrosides.

The components to which the ready autoxidation of fish oils is mainly due are polyethenoid acids of the C_{18}, C_{20}, C_{22}, C_{24}, and even, perhaps, C_{26} series, those of the C_{20} and C_{22} groups being by far the most abundant. Clupanodonic acid, belonging to this series, was isolated by Tsujimoto [17] in 1906 from Japanese sardine oil and at first believed to be a C_{18} acid; but in 1920 he stated that its formula was $C_{22}H_{34}O_2$ (a docosapentaenoic acid). Subsequently a number of other individual polyethenoid acids have been reported, including stearidonic,[18] $C_{18}H_{28}O_4$ (octadecatetraenoic), arachidonic, $C_{20}H_{32}O_2$ (eicosatetraenoic, also present in small amounts in many land animal liver and depot fats), and, in very small quantities in certain fish oils, hiragonic acid,[19] $C_{16}H_{26}O_2$ (hexadecatrienoic), nisinic,[20] $C_{24}H_{36}O_2$ (tetracosahexaenoic), shibic,[21] $C_{26}H_{42}O_2$ (hexacosapentaenoic), and thynnic,[21] $C_{26}H_{40}O_2$ (hexacosahexaenoic) acids. The constitution of these polyethenoid acids has been the subject of much investigation, but cannot yet be regarded as settled.*

The detailed description of the component acids of fish oils (in which, it should be noted, the unsaturated acids are placed in their homologous groups with a general statement of their mean unsaturation) will be dealt with in several categories, following where possible the zoological classification of the fish.

* *Cf.* Chapter IX, pp. 433–435.

Liver fats of (marine) Elasmobranch fish. Table 3 (p. 33) shows the quantitative data which have been recorded for some liver oils of this subdivision of fish. (The figures have in all cases been rounded off to the nearest unit or half-unit.)

The component acids of the Elasmobranch fish liver oils shown in Table 3 exhibit considerable variation in type, but those which contain very small proportions of unsaponifiable matter (1–2 per cent.) are typically " marine " in type, with large proportions (ca. 50 per cent.) of unsaturated C_{20} and C_{22} acids, of which the mean unsaturation is very high. Tsujimoto[30] has classified liver fats of the Elasmobranchii in three broad groups according to their content of " unsaponifiable matter " and the nature of the latter :

(*a*) Those of which the unsaponifiable content is very small (1–2 per cent.) and consists mainly of sterols.

(*b*) Those containing moderate amounts of unsaponifiable matter (10–35 per cent.), which in these cases is made up of some cholesterol with considerable proportions of the glyceryl ethers known as selachyl, chimyl, and batyl alcohols. *

(*c*) Those containing very large amounts of unsaponifiable matter which, in addition to some quantity of the glyceryl ethers just mentioned, is also usually rich in the terpenoid hydrocarbon squalene.†

The liver fats in Table 3 are given in increasing order of their contents of " unsaponifiable matter," the nature of which in each case is as follows :

LIVER FAT FROM	UNSAPONIFIABLE MATTER	
	PER CENT.	APPROXIMATE COMPOSITION
Skate	0·3	Mainly cholesterol
Angel fish	1·5	,, ,,
Thresher shark	1·8	,, ,,
Spotted dogfish	2	,, ,,
Grey dogfish	10	Mainly selachyl, with some chimyl and batyl alcohols.[30]
Ratfish	37	Almost wholly selachyl, with some chimyl and batyl alcohols.
Shark species	50–80	Large amounts of squalene with some selachyl, etc., alcohols.

The change in the character of Elasmobranch fish liver oil component acids (which consists in marked diminution of the polyethenoid unsaturation, together with some diminution in the total amounts of C_{20} and C_{22} acids and the appearance of a certain amount of unsaturated C_{24} (selacholeic) acid) sets in almost exactly parallel with the appearance of unusually large proportions of selachyl and the related alcohol-ethers. Hilditch and Houlbrooke,[25] followed by Guha *et al.*,[22] correlated this with the presence of squalene in increasing proportions (the latter authors attributing a small squalene content to the grey dogfish oil, which other workers [29, 30, 31] have shown to be absent from this fat). Lovern [31] has pointed out that, since neither the grey dogfish nor the ratfish liver oils contain any squalene, the connection between squalene and the fatty acid type (always difficult to understand) breaks down. In place of it he suggests the more consistent view that disappearance of polyethenoid unsaturation in the higher fatty acids, accompanied by appearance of alcohol-ethers of the selachyl type, are both to be regarded as evidence of an unusual tendency towards saturation or hydrogenation in this group of fish liver oils. The production of these alcohol-ethers, which must have been synthesised in the fish, can be most readily "pictured by a hydrogenation of the glyceride molecule affecting the carbonyl group." Lovern also draws attention to the unusual appearance of small amounts of arachidic and (in ratfish liver oil) even behenic acid in some of the oils in question, a circumstance equally suggestive of unusual tendency towards hydrogenation.

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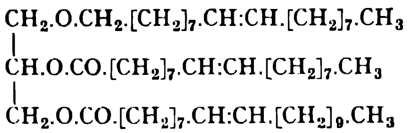
* Selachyl alcohol, α-Δ^9-octadecenylglyceryl ether, $CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.CH_2.O.CH_2.CH(OH).CH_2(OH)$.

Chimyl alcohol, α-hexadecylglyceryl ether, $CH_3.[CH_2]_{14}.CH_2.O.CH_2.CH(OH).CH_2(OH)$.

Batyl alcohol, α-octadecylglyceryl ether, $CH_3.[CH_2]_{16}.CH_2.O.CH_2.CH(OH).CH_2(OH)$. (*Cf.* Chapter X, pp. 459–461.)

† The hydrocarbon squalene, $C_{30}H_{50}$ (Chapter X, p. 443), was found by Tsujimoto[27] in the livers of 16 out of 36 species examined of Elasmobranch fish from Japanese waters. It was present chiefly in the liver oils of some members of the family Squalidæ, and also in certain members of the Cetorhinidæ, Chlamydoselachidæ, Dalatiidæ, and Scylliorhinidæ, and in the eggs of two of the species in which it was present in the livers. Heilbron, Kamm, and Owens[28] also observed it in comparatively undeveloped eggs of *Etmopterus spinax* (Squalidæ), but not in the more developed ova. Channon[29] found squalene present in the livers of 3 members of the Squalidæ (*Spinax niger*, *Scymnorhinus lichia*, and *Lepidorhinus Iguanosus*) but absent from those of 2 other members of the family and of 11 members of other Elasmobranch families ; it was also absent from

It was shown by André and Bloch [32] that the glyceryl ethers almost certainly are not present in the free condition, but occur in the liver oils as fatty acid esters. A very large proportion of ratfish liver oil, containing over 30 per cent. of these ethers, will therefore consist of di-acyl esters of selachyl, chimyl, and batyl alcohols, a possible instance of which would be, for example:



$$\begin{array}{ll} CH_2.O.CH_2.[CH_2]_7.CH{:}CH.[CH_2]_7.CH_3 & \text{Octadecenyl alcohol} \\ | & \\ CH.O.CO.[CH_2]_7.CH{:}CH.[CH_2]_7.CH_3 & \text{Oleic acid} \\ | & \\ CH_2.O.CO.[CH_2]_7.CH{:}CH.[CH_2]_9.CH_3 & \text{Gadoleic acid} \end{array}$$

It remains to be seen, of course, how far these generalisations (based on what are, after all, a very few instances) will be modified as more data are collected for fish of other Elasmobranch species; so far as they go, however, they form a steadily progressive series in the sense which has been indicated. Many of the analyses in Table 3, as well as the interpretation which at present holds the field, are due to the work of Dr. Lovern at the Torry Research Station, Aberdeen, of the Food Investigation Board, who is also responsible for a considerable proportion of the data with which the rest of this chapter is occupied. Reference may be made here to his monograph on "The Composition of the Depot Fats of Aquatic Animals." [78]

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14 species of Teleostid fish examined and from various phyto- and zoo-plankton. The occurrence of squalene thus appears to be comparatively limited, even in the Elasmobranchii, and to be somewhat erratic within individual families in this group.

Squalene is frequently accompanied by much smaller proportions of an *iso*octadecane (pristane [76]) and possibly an octadecene, $C_{18}H_{36}$.

Hata and Kunisaki [77] have reported that the liver oil of a small species of deep sea Formosan shark contained 87·5 per cent. of unsaponifiable matter, of which 84 per cent. was hydrocarbons, chiefly squalene.

TABLE 3. *COMPONENT ACIDS (WTS. PER CENT.) OF LIVER FATS OF (MARINE) ELASMOBRANCH FISH*

FAMILY	SPECIES	" UNSAPONIFIABLE MATTER " IN OIL (Per Cent.)	SATURATED				UNSATURATED					
			C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
Rajidæ	Skate *Raia maculata* [22]	0·3	4·0	14·0	—	—	Trace	10·5 (−2·0H)	20·5 (−3·3H)	32·5 (−7·3H)	18·5 (−9·5H)	—
Squatinidæ	Angel fish *Squatina angelus* [23]	1·5	1·4	17·0	2·0	—	—	6·5 (−2·0H)	20·7 (−3·0H)	21·9 (−6·0H)	30·5 (−10·2H)	—
Alopiidæ	Thresher shark *Alopæcia vulpes* [24]	1·8	7·4	11·3	0·2	—	1·6	12·0 (−2·0H)	19·2 (−3·4H)	31·0 (−6·6H)	17·3 (−10·5H)	—
Scylliidæ	Small spotted dogfish *Scyllium canicula* [23]	2	1·7	15·7	3·3	—	—	4·0 (−2·2H)	25·3 (−3·0H)	24·4 (−6·4H)	24·8 (−9·2H)	Trace ?
	*Large spotted dogfish [24] *Scyllium catulus*	?	3·2	15·7	2·0	—	1·7	12·6 (−2·0H)	40·3 (−2·8H)	10·7 (−6·0H)	13·8 (−10·4H)	—
Squalidæ	Grey dogfish *Squalus acanthias* [22]	10	6·0	10·5	3·0	—	—	9 (−2·0H)	24·5 (−2·3H)	29 (−3·3H)	12 (−4·0H)	6 (−2·0H)
Chimæridæ	Ratfish *Chimæra monstrosa* [23]	37	—	8·4	7·2	1·3 (*a*)	—	2·5 (−2·0H)	50·6 (−2·2H)	19·6 (−2·9H)	7·9 (−3·5H)	2·1 (−?H)
Squalidæ	Shark sp. *Centrophorus*, etc., sp. [25]	50–80	1·0	13·2	1·3	1·2	0·2	3·5 (−2·0H)	35·4 (−2·1H)	16·4 (−2·2H)	15·8 (−2·3H)	12·0 (−3·0H)
Squalidæ	Shark sp. *Scymnorhinus lichia* [26]	70–80	1·2	14·6	3·6	0·8 (*b*)	0·4	3·7 (−2·0H)	29·1 (−2·0H)	10·6 (−2·0H)	25·9 (−2·1H)	10·0 (−2·0H)

(*a*) Also 0·4 per cent. C_{22}.

(*b*) Also 0·1 per cent. C_{22}.

* From South African coast.

The characteristics of many other liver oils of the Elasmobranchii (especially Asiatic varieties of shark and related fish), and mention of various individual acids or groups of acids therein present, are to be found in numerous studies by Tsujimoto and other Japanese investigators, especially since about 1925 ; but unfortunately any indication of the relative proportions or other quantitative aspects of the component fatty acids is rarely, if ever, included in their work. This is the more to be regretted, since what is clearly needed is amplification of the still somewhat sparse quantitative data existing in this field. Tsujimoto [30] has, for example, found reason to believe that a fourth class of Elasmobranch fatty acids may occur in some cases: for the liver oil of a white shark (*Carcharias gangeticus*, family Galeidæ) which contains 12–35 per cent. of "unsaponifiable matter" (mainly alcohols of the selachyl group) was found by him to be remarkably low in unsaturation. Its component acids included approximately 50 per cent. of saturated (mainly palmitic) with 50 per cent. of unsaturated (almost wholly hexadecenoic and oleic) ; the total amount of C_{16} (palmitic and hexadecenoic) acids is thus extraordinarily large in this case. (In the cases recorded in Table 3, it will be noticed that the saturated acid contents are relatively constant, the hexadecenoic figure usually low, whilst the amount of unsaturated C_{18} acids, which is 20–25 per cent. of the whole in the oils of most typically "marine" type, rises in one instance to as much as 50 per cent.)

Another instance of a fat belonging to this fourth class is the oil which forms over 40 per cent. of the liver of the fan-fish (*Dasyatis akijei*, family Dasyatidæ) and contains 8 per cent. of unsaponifiable matter ; according to Wang and Kan,[33] the component acids of the fat include palmitic 19, stearic 46, oleic and other unsaturated C_{18} acids 30 ($-3{\cdot}6H$), and unsaturated C_{20} and C_{22} acids 5 per cent.

Liver fats of marine Teleostid fish. In some families of this division of fish, the livers contain large amounts of fat and act as the main fat store of the fish, but in others, especially Clupeidæ, the livers are small and/or have only small fat contents whilst the flesh may contain considerable amounts of depot fat. In fish livers which contain much fatty matter, the latter is almost wholly glycerides: the content of phosphatides in these liver oils is usually very low, and the amount of non-fatty or unsaponifiable matter (mainly cholesterol) is also small, usually not exceeding 1 per cent. of the oil (for a classification of fish according to the amount and nature of the unsaponifiable matter of the liver oils, *v.* Evers and Smith[34]).

Table 4 (pp. 36, 37) gives a summary of data which have been published for the quantitative composition of the mixed fatty acids of fats from the livers of various marine Teleostid fish ; but a few examples (e.g. liver fats of eels, salmon, and sturgeon) are reserved for special notice after some of the fresh-water Teleostid fish liver oils have been discussed. (Where the figures are from recent work, they are given as published, i.e. to the first decimal place ; this does not, of course, mean that they are necessarily accurate to within more than 1 unit per cent., while in certain circumstances the experimental error may be somewhat greater than this.)

The figures in Table 4 suggest that in many cases the following represent the proportions of the major component acids in marine Teleostid fish liver oils: palmitic, 10–15 ; hexadecenoic, 12–18 ; unsaturated C_{18} (mean unsaturation ca. $-3H$), 25–30 ; unsaturated C_{20} (mean unsaturation ca. $-6H$).

25–30; and unsaturated C_{22} (mean unsaturation ca. —7H), 10–15 per cent.* A statistical survey by Lovern [23] of the data for the component acids of liver and body oils of marine and fresh-water fish bears out the broad differences in the component acids of fish fats of respective marine and fresh-water origin (typical analyses of fresh-water fish fatty acids are given in Table 6, p. 42); the typical percentages of unsaturated acids revealed by the statistical analysis of results for fats of marine origin were C_{16}, 10; C_{18}, 25; C_{20}, 25; and C_{22}, 15. Whilst these proportions are on the whole typical, and are indeed closely adhered to in quite a number of instances, it is clear from inspection of Table 4 that there are many subordinate variations. The possible incidence of various factors—food, salinity, species characteristics, etc.— has been discussed in some detail by Lovern in the papers cited in Table 4, and we shall return to the subject later (pp. 43, 48, 49). For the present we shall merely draw attention to the chief instances in Table 4 which seem to depart from the typical compositions.

Perhaps the most marked differences are to be seen, so far, in the fatty acid compositions of liver oils of fish inhabiting the seas respectively surrounding New Zealand and Great Britain; for some reason at present unknown, it would appear that some of the New Zealand liver oils tend rather towards the typical composition of a fresh-water fish liver oil (*cf.* Table 6, p. 42), and diverge somewhat from that most frequently encountered in the marine fish liver oils of the North Atlantic. This is not wholly the case, and the liver oils of the New Zealand red cod and hake, for example, belong definitely to what, following Lovern, we may term the "marine" type. Moreover, the differences referred to are mainly increase in unsaturated C_{18} acids at the expense of the C_{22} (and sometimes the C_{20}) group; hexadecenoic acid is usually subnormal in amount, whereas in fresh-water fish fats its proportion is generally notably increased.

Studies by Rapson, Schwartz and van Rensburg [90a] on fish (stockfish and jacopever) from the South Atlantic and Southern Indian oceans bordering the western and eastern coasts of South Africa have revealed resemblances in the component acids of their liver fats to those of New Zealand fish. It would thus appear that liver oils of marine fish from the Southern Hemisphere as a whole differ slightly in their component acids from those of fish inhabiting the Northern Hemisphere, the main difference being enhanced contents of unsaturated C_{18} acids in the first-named class. It may be added that these authors have observed that fish from the Western coasts of South Africa reach maximum fat content in winter (June–July), whilst those from the eastern coasts attain maximum fat content in the summer (December) and have correlated this with characteristic differences in mean temperature, relative abundance of phyto- and zoo-plankton, and other

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* *Unsaturation of the polyethenoid C_{18}, C_{20}, and C_{22} acids.* As already mentioned, the unsaturated C_{20} and C_{22} acids of fish oils include, in addition to a certain quantity of mono-ethenoid acids, polyethenoid acids containing probably five or six ethylenic groups in the molecule; but di- and tri-ethenoid acids of these series have not been so far reported. Similarly, the unsaturated C_{18} acids of cod liver and whale blubber oil, according to Green and Hilditch,[41] are made up of mono-ethenoid (chiefly oleic) and tetra-ethenoid derivatives, but ordinary linoleic acid is either absent, or present in only minor amounts. Small proportions of polyethenoid C_{16} acids occasionally accompany hexadecenoic acid in some of the fish oils, and Toyama and Tsuchiya [19] have identified a triethenoid acid $C_{16}H_{26}O_2$ ("hiragonic acid") in the case of Japanese sardine oil.

TABLE 4. *COMPONENT ACIDS (WTS. PER CENT.)*

FAMILY	SPECIES	HABITAT	OIL IN LIVER (Per Cent.)	" UNSAPONIFIABLE MATTER IN OIL (Per Cent.)
Gadidæ	Cod (*Gadus morrhua*)	Newfoundland [22]	40–65	0·8–1
		Norwegian [22]	,,	,,
		North Sea [23]	,,	,,
		,, ,, [35]	,,	,,
		,, ,, [36]	,,	,,
	Coalfish, saith [22] (*G. virens*)	,, ,,	40–60	0·7–1
		,, ,,	,,	,,
	Pollack [23] (*G. pollachius*)	,, ,,	ca. 70	
	Haddock [37] (*G. æglefinus*)	,, ,,	ca. 70	0·7
	Red cod [38] (*Physiculus bachus*)	New Zealand, Cook Strait.	23	2·7
	Ling [22] (*Molva molva*)	North Sea	ca. 70	1·1
	Hake [22] (*Merluccius merluccius*)	,, ,,	ca. 50	1·3
		,, ,,		
	New Zealand hake [38] (*Merluccius gayi*)	New Zealand, Cook Strait.	23	3·3
	Stockfish [9ob] (*Merluccius Capensis*)	S. Atlantic, South African coast.	40–50	2·5–3·0
Serranidæ	Groper † (liver glycerides) [38] (*Polyprion oxygeneios*)	New Zealand, Cook Strait (*a*)		3·3
		,, ,, (*b*)	9	5·8
		,, ,, (*c*)	8	12·3
Scorpænidæ	Jacopever [9ob] (*Sebastichthys Capensis*)	S. Atlantic, South African coast.	2·5–40	7–11
Blenniidæ	Catfish [28] (*Anarrhichas lupus*)	North Sea	ca. 30	4–5
Ophidiidæ	New Zealand Ling[39] (*Genypterus blacodes*)	New Zealand, Cook Strait.	35–40	
		,, ,,		
Scombridæ	Tunny [40] (*Thynnus thynnus*)	North Sea	20–25	1–8 (?)
Pluronectidæ	Halibut [37] (*Hippoglossus vulgarus*)	,, ,,	ca. 20	6·6
	Turbot [23] (*Rhombus maximus*)	,, ,,	ca. 20	8·0
Lophidæ	Angler (Monk) fish [37] (*Lophius piscatorius*)	,, ,,	30–50	1

* Ueno and Matsuda [41] found that the completely hydrogenated acids of an Alaskan pollack liver oil consisted of C_{14} 1, C_{16} 13–14, C_{18} 37–38, C_{20} 18–19, C_{22} 25–26, and C_{2} 1 per cent.

OF LIVER FATS OF MARINE TELEOSTID FISH

Saturated			Unsaturated					
C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
6	8·5	0·5	Trace	20 (−2H)	29 (−3H)	26 (−6H)	10 (−7H)	—
5	6·5	Trace	0·5	16 (−2H)	31 (−3H)	30·5 (−5H)	10·5 (−?H)	—
3·5	10	—	0·5	15·5 (−2H)	25 (−3H)	31·5 (−6H)	14 (−7H)	—
4	11	1	Trace	11 (−2H)	27 (−2·5H)	27 (−5H)	19 (−7H)	—
2	14	1	2	10 (−2H)	26 (−3·3H)	25 (−5·5H)	20 (−7·4H)	Trace
6·5	13	0·5	—	14·5 (−2H)	31 (−3H)	24·5 (−?H)	10 (−?H)	—
6	12	Trace	Trace	9·5 (−2H)	29·5 (−3H)	26·5 (−5H)	16·5 (−7H)	—
2·1	13·0	1·4	—	10·9 (−2H)	34·2 (−2·7H)	25·4 (−5·4H)	13·0 (−6·5H)	—*
4·3	14·1	0·3	0·5	12·4 (−2H)	30·5 (−2·6H)	29·3 (−6H)	8·6 (−7·3H)	—
1·6	14·4	3·1	—	7·7 (−2H)	30·7 (−3·0H)	28·2 (−6·6H)	14·3 (−10·3H)	—
5	13	1	Trace	13 (−2H)	32·5 (−3H)	24 (−6H)	11·5 (−7H)	—
7	13	—	Trace	17 (−2H)	18 (−3H)	31 (−5H)	14 (−?H)	—
4·5	12	0·5	—	12 (−2H)	27 (−3H)	30 (−4H)	14 (−6H)	—
2·1	18·4	1·2	—	9·3 (−2H)	37·3 (−2·6H)	21·0 (−5·7H)	10·7 (−8·0H)	—
1·4	17·9	1·9 §	0·4	11·8 (−2H)	32·6 (−3·3H)	19·3 (−7·1H)	12·0 (−9.0H)	2·3 (−?H)
2·4	23·0	3·4	1·6	23·3 (−2H)	39·3 (−2·5H)	7·0 (−5·9H)	Trace	—
1·9	19·3	3·3	0·1	17·3 (−2H)	45·2 (−2·3H)	9·1 (−6·3H)	3·8 (−6·3H)	—
2·0	22·7	3·3	0·2	18·2 (−2H)	40·8 (−2·4H)	8·8 (−6·0H)	4·0 (−6·0H)	—
1·2	11·6	3·9 ‡	0·6	13·5 (−2H)	46·3 (−2·3H)	12·7 (−6·3H)	7·5 (−8·7H)	2·4 (−?H)
1·5	17·9	2·3	—	11·7 (−2·2H)	46·8 (−2·6H)	12·0 (−6·4H)	5·9 (−8·2H)	1·9 (−?H)
1·1	16·4	2·6	0·1	6·3 (−2H)	37·4 (−2·2H)	21·9 (−5·3H)	14·2 (−9·0H)	—
1·9	16·1	2·7	1·1	6·1 (−2H)	34·5 (−2·1H)	24·2 (−5·3H)	13·4 (−8·5H)	—
—	17·9	8·9	—	3·4 (−2·5H)	23·5 (−2·8H)	28·2 (−5·5H)	18·1 (−7·4H)	—
3·9	15·1	0·5	—	18·7 (−2·0H)	34·4 (−2·0H)	13·8 (−5·5H)	13·6 (−7·6H)	—
7·6	14·9	0·8	1·5	21·4 (−2·1H)	27·1 (−2·5H)	14·0 (−6·1H)	12·7 (−6·7H)	—
4·9	9·6	1·3	0·4	12·1 (−2H)	30·9 (−3·5H)	24·9 (−6H)	15·9 (−8·6H)	—

† Liver glycerides of groper taken in (*a*) spring 1934 (October), (*b*) early winter 1935 (June), and (*c*) late winter, 1935 (August). See also below, p. 48.

§ Also 0·4 per cent. arachidic acid.

‡ Also 0·3 per cent. arachidic and 0·1 per cent. behenic acid.

factors which differ respectively for the South Atlantic and the southern Indian oceans.

Amongst other irregularities in Table 4 we may note the very low content of hexadecenoic acid in tunny liver oil, and the unusually low proportions of C_{20} acids in halibut and turbot liver oils, together with the almost complete absence of acids more unsaturated than mono-ethenoid in the unsaturated C_{18} acids of halibut liver oil. There is, however, one feature which differentiates halibut and turbot liver oils from the remainder of the oils in Table 4 ; in these two fish the liver is not the main storage depot of fat, which is chiefly laid down in their body tissues. As will be seen in Table 5, the body fats of halibut and turbot conform to the typical " marine " type.

One of the northern fish so far examined, the catfish, shows very similar divergences from what is, perhaps, the normal type of liver fat to those displayed in some of the New Zealand liver oils (*cf.*, for example, the New Zealand ling liver oil) ; it also has some points in common with certain Elasmobranch liver oils.

Perhaps all that can usefully be said about the relatively few detailed analyses yet available is that a normal or typical composition of the mixed fatty acids seems certainly to characterise many liver oils of marine Teleostid fish, but that many subordinate deviations from this type may occur. The chief utility of the information so far obtained will reside in the encouragement it may offer to other workers further to develop this interesting, although very difficult and tedious, branch of the natural fats ; the accumulated data from many similar investigations on different fish species cannot fail to lead to useful and, quite probably, unusually interesting results.

Body fats of marine Teleostid fish. The occurrence of depot fats in the flesh of fish is on the whole less common than in the livers, and the data available are consequently even more scanty than in the latter case. Most of the detailed analyses yet recorded are collected in Table 5 (pp. 40, 41).

The data in Table 5, although comparatively few in number, include those for fishes of widely differing kinds and families ; but on the whole the composition of the flesh fats appears to be more regular than in the case of the Teleostid liver fats—species differences are less pronounced. The major component acids in most cases fall within the following limits : palmitic, 15–18 ; unsaturated C_{16} (mean unsaturation ca. $-2{\cdot}5H$), not exceeding 10 ; unsaturated C_{18} (mean unsaturation ca. $-3H$), 20–25 ; unsaturated C_{20} (mean unsaturation ca. $-5H$), 22–26 ; and unsaturated C_{22} (mean unsaturation ca. -5 to $-7H$), 18–22 per cent. Thus the hexadecenoic acid percentage is distinctly lower, whilst the amount of unsaturated C_{22} acids is higher than is usual in typical marine fish liver fats. The proportions of unsaturated C_{18} and C_{20} acids, and also the degree of average unsaturation of the C_{20} acids, is rather lower than in most of the liver fats.

The flesh fats of the herring family (Clupeidæ) form a good illustration of these general features. The menhaden fat, however, is apparently somewhat more like the typical fat of a fresh-water fish (*cf.* below, p. 42) than the rest. The analysis of pilchard fat by Brocklesby [44] is remarkable for a high content of highly unsaturated C_{24} acids, which has not been observed in Teleostid fats by other workers ; thus Lovern [23] states that in his experience C_{24} acids only occur in appreciable amounts in a limited range of (Elasmobranch) fish fats. Lovern [43] has examined the composition of the body fats of herrings, both during the period (May–July) when the fish are feeding vigorously and largely increasing the amount of flesh fat, and subsequently. The results (quoted in Table 5) show no very great alteration in the percentages of the various homologous groups of acids as the fat content increases, except that there is a certain increase in C_{20} acids balanced by a corresponding fall in the amount of C_{22} acids, and a smaller rise in unsaturated C_{16} acids roughly balanced by a decrease in palmitic acid. On the other hand, there is a very marked rise, during the period of intensive deposition of fat, in the degree of average unsaturation of the C_{18} and C_{20} acids, and some increase in that of the unsaturated C_{16} acids ; at the same time, the mean unsaturation of the C_{20} and C_{22} groups is distinctly lower than in most fish oils.

By fractionation of the fatty acids from about a ton of Japanese herring oil, Nobori [79] showed that, in addition to myristic acid, the acids contained very small proportions of lauric, decanoic and octanoic acids ; he also found traces of these lower saturated acids in Japanese sardine oil.

The component acids of the body fats of tunny, halibut, and turbot also conform closely with the usual type (the total content of saturated acids in both tunny body and liver fats is somewhat above the average) ; it has already been pointed out (p. 38) that the liver fats of the halibut and turbot differ somewhat in composition (especially in high hexadecenoic and lower C_{20} and C_{22} acid contents) from the body fats.

The same similarity in component acids is displayed in the body fats of the mature salmon and sea-trout, but in the corresponding fats of a fresh-water fish (brown trout), or of the lampern which frequents both fresh and salt water, a change in composition is at once apparent, the percentages of C_{20} and, especially, C_{22} acids falling, whilst that of the unsaturated C_{18} acids increases considerably, as also does the degree of average unsaturation of the C_{22} acids. We shall refer to this alteration again after discussing typical fresh-water fish fats, when it will be appropriate to consider Lovern's survey [47] of the fats of the salmon at all stages of its life-cycle, which includes both fresh-water and marine conditions.

An outstanding exception in the flesh fats of marine Teleostids appears to exist in the castor oil fish, *Ruvettus pretiosus*. This is a large deep-sea fish belonging to the family Gempylidæ, which resembles a perch in appearance but grows to a length of 6 feet and a weight of about 100 lb. It is found in warm seas in the Atlantic and Mediterranean regions, and its flesh has a high fatty content. Cox and Reid [80] found that the oil contained only traces of glycerides and was substantially a liquid wax, the fatty acids being combined with a mixture of alcohols (cetyl 50 per cent., octadecyl 6 per cent., oleyl 44 per cent). The composition of the acids was also peculiar, no unsaturation higher than mono-ethenoid being observed. The chief component acid was oleic (75 per cent.), with about 13 per cent. of a hydroxy-oleic acid and 1–3 per cent. each of stearic, and of mono-ethenoid C_{20} and C_{22} acids.

This occurrence of a wax-ester type of oil in the flesh of a marine Teleostid is at present unique. As in the sperm whales (*cf.* p. 57) it is accompanied by very low unsaturation in the fatty acids of the oil ; the very high proportion of oleic acid and the presence of a hydroxy-oleic acid is also remarkable.

Fats of fresh-water fish. Lovern has examined fats (mainly body fats) from several typical British species of fresh-water fish and also from two

TABLE 5. *COMPONENT ACIDS (WTS. PER CENT.)*

Family	**Species**	**Habitat**	**Oil in Flesh (Per Cent.)**	**" Unsaponifiable Matter " in Oil (Per Cent.)**
Clupeidæ	Herring (*Clupea harengus*)	North Sea[48] April 1937	8·2	2·3
		June 1937	10·7	?
		June 1937	15·7	1·2
		July 1937	20·7	?
		October 1937	18·8	1·0
		October 1937 *	12·0	1·2
		Iceland,[81] 1942		1·4
,,	Sprat [37] (*Clupea sprattus*)	North Sea	12	1
,,	Pilchard [44] (*Sardinops cœrulea*)	Pacific		
,,	Japanese sardine [45] (*Clupanodon melanostica*)	Japan Seas	10–18	0·5–1·5
,,	Menhaden (*Brevoortia tyrannus*)	N. Atlantic [45]	10–16	0·6–1·6
		,, [82]		
		,, [83]		
		,, [95]		
Salmonidæ	† Salmon [46] (*Salmo salar*) (male)	Scotland	13·9	0·8
	(female)	,,	13·2	0·9
,,	† Sea trout [23] (*Salmo trutta*)	,,	5–10	1·2
,,	† Brown trout [23] (*Salmo trutta*)	,,	7	3·3
Scorpænidæ	Jacopever [90b] (*Sebastichthys Capensis*)	S. Atlantic (S. Africa)	3–5	3–4
Zeidæ	Cape John Dory [90c] (*Zeus Capensis*)	S. African Coast November, 1944	3·9	4·4
		June, 1945	6·2	2·3
Scombridæ	Tunny [40] (*Thynnus thynnus*)	North Sea	23	0·7
Pluronectidæ	Halibut [23] (*Hippoglossus vulgarus*)	,, ,,	4–7	1·3
,,	Turbot [23] (*Rhombus maximus*)	,, ,,	4	2·1
Petromyzonidæ (Cyclostomata)	† Lampern [23] (*Petromyzon fluviatilis*)	R. Severn (tidal)	8·5	2·3

* This specimen had recently spawned. † See also below, p. 45.

** Also 0·1 per cent. lauric acid and 0·1 per cent. arachidic acid.

§§ Also 3·6 per cent. C_{26} and higher unsaturated acids.

COMPONENT ACIDS OF FATS: FISH (BODY FATS)

OF BODY FATS OF MARINE TELEOSTID FISH

SATURATED			UNSATURATED					
C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
8·0	15·7	0·2	—	4·6 (−2·6H)	22·2 (−2·9H)	22·0 (−3·9H)	27·3 (−4·2H)	—
7·3	16·7	Trace	0·6 (−2·2H)	7·5 (−2·7H)	21·1 (−3·3H)	27·3 (−4·8H)	19·5 (−5·7H)	—
7·5	12·8	0·1	0·3	7·0 (−3·0H)	21·1 (−4·8H)	30·0 (−5·2H)	21·2 (−4·8H)	—
8·3	12·1	0·3	0·5	6·4 (−3·4H)	21·0 (−4·5H)	28·3 (−5·5H)	23·1 (−4·6H)	—
7·3	13·0	Trace	0·8	4·9 (−2·7H)	20·7 (−4·2H)	30·1 (−4·6H)	23·2 (−4·3H)	—
6·6	13·7	0·5	0·2	4·9 (−2·8H)	16·3 (−3·6H)	28·7 (−4·4H)	29·1 (−4·1H)	—
7·0 **	11·7	0·8	1·2 (−2·0H)	11·8 (−2·4H)	19·6 (−3·5H)	25·9 (−5·2H)	21·6 (−4·3H)	0·1 (−3·8H)
6·0	18·7	0·9	0·1	16·2	29·0 (−3H)	18·2 (−5·5H)	10·9 (−7H)	—
5·1	14·4	3·2	0·1 (−2H)	11·8 (−2H)	17·7 (−3·3H)	17·9 (−4·1H)	13·8 (−8·5H)	15·2 (−10·9H)
6	10	2	—	13	24 (−2H)	26 (−5H)	19 (−5H)	—
6	16	1·5	—	15·5	30 (−4H)	19 (−10H)	12 (−10H)	—
7·0	16·0	1·0	Trace	17·0	27·0	20·0	12·0	—
8·3	14·9	4·7	5·8	23·4 (−2·0H)	31·1 (−3·9H)	8·4 (−5·6H)	3·4 (−6·4H)	—
6·8	15·5	3·1	0·1	14·9 (−2·2H)	23·7 (−3·3H)	17·5 (−?H)	10·8 (−?H)	4·0 §§ (−?H)
3·8	15·0	2·0	0·1	10·6	28·8 (−2·8H)	23·5 (−5·5H)	16·2 (−6·9H)	—
5·0	11·3	1·1	0·5	9·1	25·7 (−2·7H)	26·5 (−4·7H)	20·8 (−6·4H)	—
2·2	17·0	4·0‡	0·1	8·8 (−2·4H)	26·3 (−3·0H)	19·7 (−6·6H)	19·0 (−9·2H)	2·4 (−?H)
3·1	19·0	4·5	0·4	11·5 (−2·6H)	38·3 (−3·9H)	15·0 (−7·8H)	8·2 (−10·1H)	—
2·6	13·8	1·8 §	2·3	12·4 (−2·0H)	28·5 (−2·4H)	21·6 (−7·0H)	16·8 (−9·5H)	—
5·6	19·6	2·0¶	2·1	7·4 (−2·0H)	23·2 (−3·6H)	20·5 (−7·3H)	14·7 (−9·8H)	1·9 (−10·0H)
3·1	15·7	4·0††	0·9	9·4 (−2·0H)	23·4 (−2·5H)	19·0 (−7·0H)	21·9 (−10·5H)	0·3 (−10·0H)
4·2	18·6	3·5	—	6·2 (−2·7H)	26·0 (−3·2H)	23·5 (−5·5H)	18·0 (−6·8H)	—
4·0	14·8	0·7	Trace	6·5 (−2·6H)	23·8 (−3·0H)	26·9 (−5·2H)	23·3 (−6·5H)	—
3·4	15·1	2·1	0·3	8·9 (−2·6H)	21·7 (−3·4H)	26·6 (−6·0H)	21·9 (−7·7H)	—
9·5	17·6	0·7	—	10·9 (−2·1H)	35·3 (−2·6H)	15·3 (−6·5H)	10·7 (−10·3H)	—

‡ Also 0·4 per cent. arachidic acid. § Also 0·2 per cent. arachidic acid.
¶ Also 0·5 per cent. lauric, 1·8 per cent. arachidic and 0·6 per cent. behenic acids.
†† Also 1·8 per cent. arachidic and 0·5 per cent. behenic acids.

TABLE 6. *COMPONENT ACIDS (WTS. PER CENT.) OF FATS OF FRESH-WATER FISH*

FAMILY	SPECIES	HABITAT		FAT (Per Cent.)	UNSAPONIFIABLE (Per Cent.)	SATURATED			UNSATURATED				
						C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Salmonidæ	Salmon [47] (*Salmo salar*)	Scotland								(see below, Table 7, p. 42)			
"	Brown trout [23] (*Salmo trutta*)	"				3·1	19·0	4·5	0·4	11·5 (−2·6H)	38·3 (−3·9H)	15·0 (−7·8H)	8·2 (−10·1H)
"	Pollan [37] (*Coregonus pollan*)	Ireland	(Muscle)		1·5	2·9	14·3	1·9	1·5	19·8 (−2·0H)	40·0 (−3·2H)	13·5 (−7·4H)	6·1 (−9·1H)
Esocidæ	Pike [37] (*Esox lucius*)	Scotland	(Muscle)		4·0	4·7	13·2	0·5	0·8	20·8 (−2·0H)	38·4 (−2·8H)	15·3 (−7·5H)	6·3 (−7·5H)
			(Mesentery)		0·1	2·9	15·0	Trace	0·5	20·2 (−2·0H)	42·4 (−3·4H)	15·1 (−6·7H)	3·9 (−8·0H)
Percidæ	Perch [37] (*Perca fluviatilis*)	"	(Muscle)		6·0	3·5	12·5	2·0	1·1	19·4 (−2·0H)	40·5 (−3·2H)	13·8 (−6·8H)	7·1 (−9·2H)
Cyprinidæ	Carp [37] (*Cyprinus carpio*)	?	(Muscle)		3·5	3·7	14·6	1·9	1·0	17·8 (−2·0H)	45·8 (−3·2H)	15·2 (−6·9H)	—
"	Grass-feeding carp [48] (*Ctenopharyngodon idellus*)	Singapore	(Muscle)	3·7	2·0	1·5	13·6	2·5	1·5	6·7 (−2·0H)	64·0 (−4·3H)	10·2 (−6·4H)	—
			(Muscle)		4·4	2·6	18·0	1·9	0·7	22·9 (−2·1H)	45·7 (−3·0H)	8·2 (−6·5H)	—
			(Mesentery)		0·7	1·9	14·7	2·5	0·2	8·0 (−2·0H)	64·6 (−3·7H)	7·6 (−6·0H)	0·5
"	Mud-feeding carp [48] (*Hypophthalmicthys nobilis*)	"		ca. 2	9·5	—	17	6	—	9·5 (−2·0H)	54 (−3·6H)	13·5 (−6·8H)	—
"	Mud-feeding carp [48] (*H. molitrix*)	"		ca. 2	2·4	0·8	21·3	1·1	0·6	17·1 (−2·0H)	49·5 (−3·0H)	9·6 (−6·7H)	Trace

species of Chinese carp which feed respectively on grass and mud; a summary of his results appears in Table 6.

The reader will find it interesting, at this point, to compare the general features of Table 6 with those of Tables 4 and 5 (marine Teleostid fish fats) and Tables 1 and 2 (fats of aquatic flora and micro-fauna).

Generally speaking, it may be said that the distinctive points in the fresh-water fish fats in Table 6 are the small proportions of unsaturated C_{22} acids, the reduced proportions (as compared with many marine fish fats) of unsaturated C_{20} acids, the predominance of unsaturated C_{18} acids (which range from about 40 per cent. upwards) and the importance of hexadecenoic acid which, in the five British fresh-water fish fats, is curiously constant at about 20 per cent. The general unsaturation in the C_{20} and C_{22} groups (when the latter is present) appears to be somewhat higher than in the corresponding groups of fatty acids from marine species. It is impossible at the present stage, as Lovern [37] has emphasised, to decide how far the typical, as distinct from subordinate species, differences between marine and fresh-water fish fats may be due to differences in food, or in environmental and seasonal conditions; the various possibilities are, however, considered in detail in that author's communications. Whatever the causes, it may be suggestive that, in their markedly increased contents of unsaturated C_{18} acids (in which oleic acid predominates), they show some similarity with fats of the marine mammalia such as whale oil; so that this might be regarded as the first indication of the tendency to the almost exclusive prominence of oleic acid (with its chemically related polyethenoid acids) amongst the fats of the more developed land fauna and flora.

The special cases of the Asiatic grass- and mud-feeding carp [48] may be briefly noticed. The fats were of varying compositions, but C_{22} acids were uniformly absent. In two of the five examples they were fairly similar to the other fresh-water fats dealt with in Table 6, but in the other instances the proportion of unsaturated C_{18} acids was still further notably increased, whilst that of hexadecenoic acid was much reduced. Analyses of the fats present in the food of these particular fish showed no correlation with those of the carp fats, and the evidence thus furnished, for what it was worth, rather pointed to a synthesis by the fish, from carbohydrate or other material, of fatty acids of the desired type.

The component acids of Astrakhan whitefish (*Coregonus* sp., Salmonidæ) are given by Williams and Onischtschenko [84] as palmitic and stearic 24·9, oleic 49·2, "linoleic" 4·4, "linolenic" 14·0, and "clupanodonic" 7·5 per cent. (wt.).

SOME FURTHER EXAMPLES OF SPECIFIC FISH FATS

The fats of a few fishes have been studied more intensively than the majority of those enumerated in Tables 3, 4, 5, and 6. In one interesting group, that of certain fish which have both fresh- and salt-water relationships, the fats of salmon at all stages of the life-cycle have been studied by Lovern [47]; whilst eel fats and the fats from several depots of the sturgeon have been analysed. On the other hand, in some of the larger fish, including (in addition to the sturgeon) tunny, halibut, turbot, and groper, it has been possible to investigate fats from several parts of the animal instead of from only one depot (flesh or liver, as the case may be). These results are of sufficient interest to receive separate consideration at this point.

TABLE 7. *COMPONENT ACIDS (WTS. PER CENT.) OF SALMON FATS AT VARIOUS STAGES OF THE LIFE-CYCLE*

FAT	FAT (Per Cent.)	UNSAPONIFIABLE (Per Cent.)	SATURATED			UNSATURATED				
			C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Body fat of parr (Ettrick water) [47]	3·9	5·0	2·7 †	17·7	3·3	3·1 (>−2·0H)	21·7 (−2·3H)	30·0 (−3·8H)	12·9 (−8·3H)	9·9 (−10·2H)
„ „ smolt (Aberdeen harbour) [47]	1·2	18·0	2·7	14·3	5·0	0·7 (−2·0H)	7·9 (−2·0H)	32·2 (−3·2H)	19·4 (−6·7H)	17·8 (−9·4H)
Body fats of male and female salmon returning to spawn (increasing emaciation) : [47]										
1 Male	13·9	0·8	3·8	15·0	2·0	0·1	10·6	28·8 (−2·8H)	23·5 (−5·5H)	16·2 (−6·9H)
2 „	6·5	1·3	2·0	14·1	0·7	—	6·2	27·3 (−2·7H)	26·9 (−4·7H)	22·8 (−7·1H)
3 „	1·1	8·6	2·3	13·2	1·0	—	4·3	27·3 (−2·7H)	25·8 (−5·3H)	26·1 (−7·8H)
4 Female	13·2	0·9	5·0	11·3	1·1	0·5	9·1	25·7 (−2·7H)	26·5 (−4·7H)	20·8 (−6·4H)
5 „	7·3	1·3	2·2	12·5	1·6	—	7·7	27·1 (−2·8H)	28·4 (−4·7H)	20·5 (−6·8H)
6 „	3·5	2·2	1·9	10·0	1·8	—	7·8	28·5 (−2·6H)	33·2 (−4·3H)	16·8 (−6·4H)
Mature salmon :										
Liver [23]	?	?	2·7	10·9	1·6	0·7	12·3 (−2·0H)	32·8 (−2·9H)	25·8 (−5·7H)	13·2 (−7·8H)
Mesentery [23]	?	?	3·6	14·4	2·3	0·1	7·1 (−2·4H)	25·3 (−2·9H)	28·4 (−4·6H)	18·8 (−6·1H)
Salmon ova fats (in increasing order of maturity) : [47]										
No. 1 (from River Dee)	‡	8·8	3·1	16·0	0·5	0·1	12·6 (−2·0H)	23·7 (−4·0H)	27·2 (−8·0H)	16·8 (−10·4H)
No. 2 (from River Dee)	‡	7·4	2·9	13·4	0·7	0·4	10·4 (−2·0H)	25·3 (−3·2H)	28·7 (−7·2H)	18·1 (−11·4H)
No. 4 (from River Dee)	‡	6·3	1·8	13·0	2·0	—	9·9 (−2·0H)	36·7 (−2·9H)	21·3 (−7·6H)	15·3 (−11·1H)
No. 5 (from River Tweed)	‡	7·2	2·3	12·9	2·2	—	9·6 (−2·0H)	34·8 (−2·7H)	23·2 (−7·6H)	15·0 (−11·2H)
" Baggot " * (from River North Esk)	3–6	8·0	2·3	11·2	1·9	—	12·3 (−2·0H)	34·4 (−2·7H)	21·7 (−7·2H)	16·2 (−9·5H)

* " Baggots " is a term applied to ripe female fish which for some reason have not spawned.

† 0·7 per cent. lauric acid also present.

‡ Irregular, but varying from 7 to 15 per cent.

Salmon fats. It has already been shown, in Table 5, that the flesh fats of the sea trout and the brown trout conform respectively to Lovern's " marine " and " fresh-water " types of component fatty acid mixtures; these fish are now regarded as merely the migratory and non-migratory forms of the same species, *Salmo trutta*. Similarly, the lampern, a denizen of tidal estuaries known to visit both salt and fresh water, possesses a body fat more akin to the " fresh-water " than to the " marine " type. In the case of the trout, the adult fish may proceed to the sea or may remain in fresh-water streams (brown trout); the analyses given in Table 6 refer to the flesh fats of such adult fish.

The Atlantic salmon, *Salmo salar*, differs from the brown trout in that its adult life is spent in the sea until it returns to fresh water for spawning purposes. The eggs hatch out in fresh water, and for the first 1–4 years of their life the young salmon live like any other fresh-water fish. During this stage they are known as salmon parr. Each year, at an average age of 2 or 3 years, some of these fish change colour and become silvery like the adult salmon. Now called smolts, they swim downstream and right out to sea, becoming a marine species. The maturing and adult fish feed intensively in the sea, and then, as the spawning time approaches, migrate to the rivers and commence to ascend them. It is certain that from the moment of entering the rivers, if not earlier, the salmon cease feeding entirely. The journey upstream to the spawning grounds demands the expenditure of much energy, which has to be supplied mainly by reserve fat. Moreover, considerable quantities of fat accumulate in the gonads, and this fat is probably transferred from the depots (*vide infra*). Continuous depletion of the latter thus takes place. Almost all the males perish in the river, presumably from weakness and starvation, but most of the females survive until they reach the sea again. Here most of them presumably die also, as only a small percentage return to spawn a second time. The fish after spawning are known as kelts, and some of these have been found with as little as 0·3 per cent. of fat in the muscles, contrasted with 13–14 per cent. of fat in a fish fresh from the sea.

Lovern [47] made detailed analyses of the flesh fats from the young fish (parr and smolts), and from adult fish which had returned to spawn at various stages of emaciation; he also examined the ova fats at various stages of development of the eggs. The data for the different component fatty acids are collected in Table 7.

The interesting variations and transitions in fatty acid composition illustrated in Table 7 may be summed up briefly as follows:

" In the relative proportions of the various acids, the fat from the parr is typically of the fresh-water fish class, although the C_{18} acid percentage is somewhat low. . . . When the parr becomes a smolt, it becomes indistinguishable from an adult salmon except in point of size, and it proceeds to take up the normal marine life of the adult fish. Evidently its whole metabolism undergoes a change at this period. The fat which it has stored in its fresh-water life is suitable no longer, and the smolt fat examined appears to be at a transitional stage from a typical fresh-water fat to the special fat of the adult salmon. The lower fat content of the smolts compared with the parr suggests a partial withdrawal of fat to effect this change of type." (Lovern, *loc. cit.*) The body fat of the mature fish, as it returns to fresh water, is fairly typical of what we have called the " marine type " of fish body fats. In contrast to that of the parr, the content of C_{22} acids is high, and that of unsaturated C_{16} acids low, whilst the average unsaturation of all the groups of acids is definitely lower than that of those in the parr fat; the smolt fatty acids are intermediate in this respect.

The changes in the fatty acids during the (fasting) period in which the depot fat is being drawn upon are of great interest, although not very obvious, perhaps, at first sight. The average unsaturation is not greatly altered during fasting in fish of either sex. As regards group percentage proportions, it is fairly obvious that, as emaciation proceeds, myristic and unsaturated C_{16} acids show a decrease, balanced by increase in C_{22} acids (in the males) and in C_{18} and C_{20} acids (in the females). " The lack of parallel between the male and female series is possibly due to the different metabolic requirements and processes at spawning time. Another evidence of this is the higher and earlier incidence of mortality amongst the males than amongst the females." (Lovern, *loc. cit.*) These differences become more apparent if, following Lovern, we consider the total proportions (in mols. per cent.) of each group of acids containing the same number of carbon atoms (Table 8) :—

TABLE. 8 *MOLAR PROPORTIONS OF TOTAL ACIDS WITH THE SAME NUMBER OF CARBON ATOMS*

Fish Number	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
1 Male	4·7	28·5	31·2	21·8	13·8
2 ,,	2·6	23·1	28·9	25·5	19·9
3 ,,	2·9	20·1	29·4	24·6	23·0
4 Female	6·9	23·0	27·4	24·8	17·9
5 ,,	2·8	23·0	29·6	26·8	17·8
6 ,,	2·4	20·2	31·2	31·5	14·7

From Table 8 it appears that the constituents preferentially mobilised in the male series are those of low molecular weight, but in the female series this effect is much less in evidence, if indeed it exists at all. Lovern has put forward the view that such selective effects (other instances of which are observable in other marine animal fats, e.g. those of the Delphinidæ, p. 59) as between one fat depot and another may be brought about by a more ready passage of smaller molecules through the cell membranes—a kind of permeability or " molecular filtration " effect.

The mesenteric fat examined is very similar to that of the mature flesh fats, whilst the salmon liver fat appears slightly different, with somewhat increased amounts of unsaturated C_{16} and C_{18} acids, and somewhat less C_{22} acids.

In the egg fats, at early stages the percentages of the various acid groups are not significantly different from those of a salmon body fat, but the average unsaturation is increased in all cases. As development proceeds, the high degree of average unsaturation of the C_{20} and C_{22} acids is maintained, and there is a definite rise in the proportion of C_{18} acids together with a fall in their mean unsaturation. Mono-ethenoid C_{20} and C_{22} acids are absent from all the egg fats. The final result of the progressive changes in the ova fat during ripening is that it takes on some of the characteristics of a fresh-water fish fat, but it nevertheless still retains the specific nature of a salmon fat (e.g. low C_{16} and high C_{22} acid contents, in spite of increased proportions (ca. 35 per cent.) of unsaturated C_{18} acids). There is as yet little if any evidence to indicate the mechanism by which these changes are brought about, but various possibilities have been discussed by Lovern.[47]

TABLE 9. *COMPONENT ACIDS (WT. PER CENT.) OF EEL FATS*

FAMILY	SPECIES	HABITAT		OIL (PER CENT.)	UNSAPONIFIABLE (PER CENT.)	SATURATED			UNSATURATED				
						C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Anguillidæ	*Anguilla auchlandii*[49] (Fresh-water eel)	New Zealand	Body	7	0·8	2·4	15·9	0·8	—	21·2 (−2·0H)	46·3 (−2·6H)	12·9 (−6·3H)	0·5 (− ? H)
,,	*A. vulgaris*[6] (Fresh-water eel)	Scotland *	Body	9–30	1·2–2·0	4·3	16·8	2·5	0·1	8·8 (−2·2H)	39·4 (−2·5H)	20·8 (−5·6H)	7·3 (−10·2H)
						4·3	17·8	1·7	Trace	9·2 (−2·2H)	38·4 (−2·7H)	20·1 (−6·0H)	8·5 (−9·3H)
Congridæ	*Conger vulgaris*[50] (Conger eel)	North Sea	Liver	ca. 20	2·5	5·2	19·2	0·4	0·4	18·0	37·5 (−2·0H)	12·4 (−5·6H)	6·9 (−8·1H)
			Peritoneum	ca. 80	0·7	1·8	18·8	0·9	—	6·2	40·6 (−2·1H)	18·3 (−5·4H)	13·4 (−8·4H)

* The Scottish eels were taken from tidal waters, and cannot therefore be considered as denizens exclusively of fresh water.

Eel fats. Eels are in some respects opposite in behaviour to salmon, in that many species spend the greater part of their existence in fresh water, but migrate, sometimes many thousands of miles, to marine spawning grounds (e.g. the Sargasso sea in the West Indies). Analyses of eel fats are available for New Zealand and Scottish fresh-water eels, and for the liver and peritoneal fats of the conger, which lives in sea-water (Table 9).

The eel fats * do not fit very closely into either the general fresh- or salt-water types of fat. They are somewhat akin to the fresh-water fish fats in Table 6 (p. 42) as regards their high proportions of unsaturated C_{18} acids and their comparatively low contents of C_{22} acids, but the amount of hexadecenoic acid is variable and in any case not high, whilst the average unsaturation in the C_{18}, C_{20}, and C_{22} groups is much lower than in the case of most fats from fresh-water fish. The content of unsaturated C_{18} acids in the New Zealand eel is extremely large. In the conger, the peritoneum is a principal fat depot and the liver only a subsidiary one.

Lovern[6] has studied the composition of fats from eels reared mainly on diets of mussels or herrings in tanks at two different temperatures in either fresh or salt water, with the general results given in Table 10A.

TABLE 10A. *COMPONENT ACIDS (WTS. PER CENT.) OF FATS FROM EELS KEPT UNDER DIFFERENT CONDITIONS*

MONTHS	WATER	TEMP.	SATURATED			UNSATURATED				
			C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
					(i) *Eels fed on Mussel Diet*					
3	Sea	23°	3·1	19·8	4·8	0·7	5·8 (−2·4H)	42·6 (−2·7H)	15·7 (−5·5H)	7·5 (−8·0H)
6	,,	,,	3·7	17·4	3·9	—	9·5 (−2·1H)	39·6 (−2·4H)	16·8 (−5·2H)	9·1 (−8·6H)
5	Fresh	23°	3·6	17·9	2·8	Trace	6·8 (−2·3H)	39·2 (−2·6H)	22·4 (−5·8H)	7·3 (−8·0H)
6	,,	,,	4·1	19·4	2·2	—	5·7 (−2·1H)	37·5 (−2·8H)	20·6 (−5·5H)	10·5 (−9·2H)
6	,,	14°	3·3	20·5	2·7	—	11·6 (−2·4H)	39·4 (−2·7H)	16·1 (−6·3H)	6·4 (−10·0H)
					(ii) *Eels fed on Herring Diet*					
6	Sea	14°	4·8	17·6	2·6	—	9·4 (−2·2H)	41·6 (−2·4H)	16·4 (−5·8H)	7·6 (−9·1H)
6	Fresh	23°	6·0	16·5	1·1	0·6	8·3 (−2·2H)	33·9 (−2·8H)	22·6 (−5·5H)	11·0 (−7·0H)
6	,,	14°	6·4	17·1	1·3	—	6·9 (−2·4H)	31·9 (−3·0H)	22·2 (−5·4H)	14·2 (−7·5H)
					(iii) *Eels—" Control " Specimens from Dee Estuary*					
—	Brackish	—	4·3	16·8	2·5	0·1	8·8 (−2·2H)	39·4 (−2·5H)	20·8 (−5·6H)	7·3 (−10·2H)
—	,,	—	4·3	17·8	1·7	Trace	9·2 (−2·2H)	38·4 (−2·7H)	20·1 (−6·0H)	8·5 (−9·3H)

The mussel diet, which incidentally caused a loss of weight in the fish, appeared to have little influence on the composition of the eel fats ; but the herring diet resulted both in increase of weight and in modification of the eel fat component acids to a mixture intermediate in composition between that of the "control" eel fat and herring fat (for the latter, *cf.* Table 5, pp. 40, 41). The possible inferences to be drawn from this series of experiments have been fully discussed by Lovern (*loc. cit.*).[6]

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* The Scottish eels were taken from tidal waters, and cannot therefore be considered as denizens exclusively of fresh water.

Subsequently, Lovern [85] fed eels on individual fatty esters, including ethyl myristate, ethyl palmitate, and mixed ethyl esters of unsaturated eel fat acids. The changes in the eel body fats (illustrated in Table 10B) were too small, although consistent, to lead to very definite conclusions, except that, when ethyl palmitate was fed, there was a marked increase in palmitic acid content. Ethyl myristate (which was not very acceptable to the fish) caused an apparent rise in tetradecenoic acid, ethyl palmitate (which was readily accepted) caused rise in the content of hexadecenoic acid as well as of palmitic acid, and the diet of unsaturated esters led to results which suggested the hydrogenation of some hexadecenoic acid. In general, the results supported the view that both dehydrogenation and hydrogenation readily take place during the elaboration of fish depot fatty acids.

TABLE 10B. *COMPONENT ACIDS (WTS. PER CENT.) OF FATS FROM EELS FED ON SPECIFIC FATTY ESTERS*

DIET	SATURATED			UNSATURATED				
	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Control	4·3	17·3	2·1	0·1	9·0 (−2·2H)	28·9 (−2·6H)	20·4 (−5·8H)	7·9 (−9·7H)
With ethyl myristate	5·5	17·3	2·2	1·3	7·6 (−2·2H)	35·8 (−2·7H)	18·9 (−5·8H)	11·4 (−10·0H)
With ethyl palmitate	5·8	25·7	2·2	0·4	9·1 (−2·2H)	37·1 (−2·5H)	13·6 (−5·6H)	6·1 (−8·5H)
With unsaturated ethyl esters	5·4	16·0	2·1	—	6·0 (−2·2H)	42·6 (−2·6H)	20·9 (−5·2H)	7·0 (−10·5H)

FATS FROM DIFFERENT DEPOTS OF SOME LARGE FISHES

When the size of the fish permits, it has been possible in some instances to determine the component acids from several of the main depots. Some of the resulting data are considered below.

Sturgeon fats.[51] The sturgeon (*Acipenser sturio*) examined had been caught in the North Sea, but all sturgeon ascend the large continental rivers to spawn and, it is believed, do most of their feeding in fresh water. It is not surprising, therefore, to find that its fats conform in general with the fresh-water fish type, subject as usual to minor specific differences. Fat deposited in the peritoneal cavity is the chief store in the sturgeon, whilst the pancreas is also very rich in fat; the liver is not exceptionally rich in fat. The component acids of fats from these parts of the animal are tabulated in Table 11.

TABLE 11. *COMPONENT ACIDS (WTS. PER CENT.) OF FATS FROM A STURGEON*

FAT FROM	IODINE VALUE	SATURATED			UNSATURATED				
		C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Peritoneal cavity	126·5	7·1	14·0	0·8	0·6	23·8	35·8 (−2·9H)	12·1 (−7·4H)	5·8 (−8·6H)
Pancreas *	119·6	4·5	16·4	1·1	—	21·4	36·7 (−2·9H)	14·5 (−6·8H)	5·4 (−9·1H)
Liver	125	3·0	19·2	—	—	19·5	39·6 (−2·7H)	11·8 (−7·1H)	6·9 (−10·0H)

* There is some uncertainty as to whether the organ examined was the pancreas or the pyloric cæca.—(Private communication by Dr. Lovern.)

These form a specially interesting group in several respects. In the first place, it was one of the first instances—several others may be noticed in the course of the preceding and following tables—in which it was shown that the liver glycerides were no more unsaturated than the main depot fat of the same fish. Actually, the molar proportion of saturated acids is constant in all three fats (23·9, 23·8, and 24·1 per cent. respectively for the peritoneal, pancreatic,* and liver fats), whilst the average degree of unsaturation of the C_{18} and C_{20} acids is lower in the liver fat than in the main depot fat (although that of the small proportion of C_{22} acids is somewhat higher). Although the total molar content of saturated acids is constant, the individual acids vary widely (C_{14} from 3·6 to 8·4 per cent., C_{16} from 14·7 to 20·5 per cent.) ; at the same time, however, there is another curious constant feature in this series, namely, the molar percentages of the total C_{16} acids (palmitic and hexadecenoic) which are respectively 40·0, 40·3, and 41·4 per cent. in the three fats. Lovern [51] suggests that it would appear that all sturgeon fats develop an approximately constant proportion of saturated (24 per cent.) to unsaturated (76 per cent.) acids, and that this constancy may be secured by alteration in the proportions of saturated and mono-ethenoid C_{16} acids. It is only fair to add that such close numerical constancy is as yet unobserved in other fish fats, but nevertheless the relationships appear too definite to be merely fortuitous. Comparison of Table 11 with Table 6 will show the close general similarity of the sturgeon fats to the fats of the smaller, fresh-water fish.

Tunny fats. The examination of fats from various organs and the flesh of a large tunny (*Thynnus thynnus*) taken in the North Sea (off Scarborough) has also yielded interesting and suggestive results (Table 12A).[40]

TABLE 12A. *COMPONENT FATTY ACIDS (WTS. PER CENT.) OF TUNNY FATS (GLYCERIDES)*

DEPOT	FAT (Per Cent.)	SATURATED			UNSATURATED				
		C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Flesh	23	4·2	18·6	3·5†	—	6·2 (−2·7H)	26·0 (−3·2H)	23·5 (−5·5H)	18·0 (−6·8H)
Liver	20–25	—	17·9	8·9†	—	3·4 (−2·5H)	23·5 (−2·8H)	28·2 (−5·5H)	18·1 (−7·4H)
Pyloric cæca	28·5	3·4	18·4	2·7	—	6·3 (−2·7H)	21·9 (−3·7H)	25·5 (−5·5H)	21·8 (−6·2H)
Spleen	2·6	—	21	7	—	7 (>−2·0H)	27 (−3·1H)	22 (−5·4H)	16 (−?H)
Heart	2·4	—	25	3	—	4 (>−2·0H)	26 (−3·4H)	25 (−5·4H)	17 (−7·5H)

Compared with other marine fish fats, the tunny fats in Table 12A exhibit the following well marked species peculiarities : in the saturated acids, absence of myristic acid in several cases, somewhat high palmitic acid contents, presence of unusual amounts of stearic acid and of traces of arachidic acid in the liver and flesh fats ; in the unsaturated acids, absence of tetradecenoic acid, low hexadecenoic acid contents, average unsaturation perhaps somewhat lower than usual in the C_{18}, C_{20}, and C_{22} acids, and the presence of small proportions (perhaps 1–2 per cent.) of unsaturated acids of the C_{24} or higher series (included in Table 12A with the C_{22} acids). The tunny normally spends considerable periods in relatively warm water and moreover is notable for having a body temperature some 3° higher than that of the

† Traces of arachidic acid also present.

water. Lovern [40] suggests that there may be some correlation between these factors and, in particular, draws attention to progressive relationships discernible between the total content of saturated acids, the amount of stearic acid, and the degree of average unsaturation of the unsaturated C_{18} acids in the fats from various parts of the tunny (Table 12B).

TABLE 12B. *RELATION BETWEEN STEARIC ACID CONTENT AND DEGREE OF UNSATURATION OF* C_{18} *ACIDS IN TUNNY FATS*

Depot	Total Saturated Acid (Per Cent.)	Stearic (Per Cent.)	Degree of Unsaturation of C_{18} Acids
Pyloric cæca	24·5	2·7	−3·7
Heart	28	3	−3·4
Flesh	26·3	3·5	−3·2
Spleen	28	7	−3·1
Liver	26·8	8·9	−2·8

The fat of the pyloric cæca, which is likely to be largely directly ingested fat (in which stearic acid would form at most 1 per cent. of the total acids), is lowest in total saturated acids and in stearic acid content. The other four fats contain 27–28 per cent. of total saturated acids (much above the usual value, 15–20 per cent., for marine fish), and this is made up, partly by stearic acid, but mainly by a higher palmitic acid percentage than usual (18–25 per cent. as compared with the usual 8–16 per cent.). The total C_{16} acid percentage (21–29 per cent.) is of the same order as that in most fish fats, so that it is reasonable to conclude that the high palmitic acid contents are at the expense of the hexadecenoic acid contents. In other words, as Lovern has emphasised, saturation (hydrogenation) processes seem to be operative in both the C_{16} and C_{18} acids of the tunny fats. He has also drawn attention to the fact that the highest stearic acid content and lowest degree of unsaturation of the C_{18} acids appear in the liver fat; so that the tunny provides another example in which the liver fat is definitely less unsaturated than the body fats. (The liver and body fats of the conger eel, Table 9, and those of halibut and turbot, Tables 4 and 5, are other, and even better, examples in which the degree of average unsaturation and/or the actual contents of unsaturated C_{20} and C_{22} acids are markedly lower in the respective liver fats than in the body fats.)

Groper liver and head oils. The New Zealand groper, *Polyprion oxygeneios*, contains fat deposits in the liver, head, and body of the fish; according to Johnson [52] a considerable proportion of the total fat is concentrated in the body, whilst Shorland and Hilditch [38] state that the amount in the head is about four times that in the liver, which is therefore in this case a secondary depot for fat. The latter authors have examined groper liver and head oils (data for the groper liver glycerides have already been mentioned in Table 4). The liver oils vary considerably, according to the season, in their contents of vitamin A, unsaponifiable matter, and phosphatides; this will be evident from the figures in Table 13.

The groper liver oils seem to have definite species peculiarities, but that from the head (which, as has been pointed out, is one of the principal fat depots) is quite similar to many of the fats in Tables 4 and 5 which represent main depots in many other marine fish. The groper liver glycerides are characterised by low proportions of unsaturated C_{20} and (especially) C_{22} acids, with high palmitic, hexadecenoic and unsaturated C_{18} acids (the mean unsaturation of the latter being comparatively low). The total content of C_{16}

TABLE 13. *GENERAL COMPOSITION OF GROPER FATS*

SOURCE	FATTY CONTENT OF ORGAN (Per Cent.)	FATTY EXTRACT			
		IODINE VALUE	UNSAPONIFIABLE (Per Cent.)	GLYCERIDES * (Per Cent.)	PHOSPHATIDES (Per Cent.)
Liver (spring)	?	88·6	3·3	100	Trace
,, (early winter)	9·2	87·0	5·8	98	2
,, (late winter)	8·0	112·2	12·3	82	18
Head	8·0	145·9	0·7	100	Trace

* I.e. glycerides+unsaponifiable matter, but excluding phosphatides.

COMPONENT ACIDS (WTS. PER CENT.) OF GROPER LIVER AND HEAD FATS

	SATURATED			UNSATURATED				
	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Liver glycerides :								
Spring	2·4	23·0	3·4	1·6 (−2·0H)	23·3 (−2·0H)	39·3 (−2·5H)	7·0 (−5·9H)	Trace
Early winter	1·9	19·3	3·3	0·1	17·3 (−2·0H)	45·2 (−2·3H)	9·1 (−6·3H)	3·8 (−6·3H)
Late winter	2·0	22·7	3·3	0·2	18·2 (−2·0H)	40·8 (−2·4H)	8·8 (−6·0H)	4·0 (−6·0H)
Liver phosphatides (late winter)	←—— 18·5 ——→			—	16·9 (−2·0H)	19·6 (−2·4H)	31·1 (−6·6H)	13·9 (−?H)
Head glycerides	3·0	16·0	3·1	1·1 (−2·0H)	13·8 (−2·0H)	30·8 (−2·6H)	18·5 (−6·2H)	13·7 (−9·2H)

acids in the liver glycerides is remarkably high, 36–46 per cent., as is also the total percentage (24–29) of saturated acids. In some respects, these liver glycerides resemble typical fresh-water, rather than marine, fish liver fats ; but they are sharply differentiated from the former by the high proportions of palmitic acid and the lower contents of unsaturated C_{20} acids.

The liver phosphatides, on the other hand, show the usual features in fatty acid composition as compared with the corresponding glycerides, notably, greater amounts of unsaturated C_{20} and C_{22} acids and correspondingly less unsaturated C_{16} and C_{18} acids. Similar comparative differences in the component acids have been observed by Shorland [39] in the roe glycerides and phosphatides of the New Zealand ling (*Genypterus blacodes*). These appear to be general features in nearly all animal liver phosphatides, and we shall encounter other instances which have been examined in more detail in the case of land animal fats (Chapter III, pp. 106–110).

The similarity of the component acids of the groper head oil to those of the fats from the main fat depots (body or liver) of other marine fish has already been mentioned. It will be seen below, however, that in the case of certain of the larger marine mammals the fat depots in the head of the animal are characterised by the presence and concentration of acids of lower molecular weight than those found in the liver, or even the body, fats of the same animal. If, therefore, the state of affairs in, for example, the sperm whale or the porpoise could be taken as the normal, the composition of the groper head oil—although it conforms with the average for a typical marine fish main depot fat—would appear to be unusual for a fat from the head of a marine animal. Of course, out of the few instances which have yet been investigated, it is not practicable to say which is the more normal type.

TABLE 14A. *GENERAL COMPOSITION OF SOUTH AFRICAN FISH FATS*

FAMILY		HABITAT	HEAD			BODY			LIVER			VISCERA		
		(Ocean)	Wt. (Per Cent.)	Fat (Per Cent.)	I.V.	Wt. (Per Cent.)	Fat (Per Cent.)	I.V.	Wt. (Per Cent.)	Fat (Per Cent.)	I.V.	Wt. (Per Cent.)	Fat (Per Cent.)	I.V.
Scorpænidæ	Jacopever (*Sebastichthys Capensis*)	S. Atlantic	22–25	9–13	150–160	67–70	3–5	150–160	1·5–3.0	25–40	110–135	2·0–2·5	20–30	145–160
Serranidæ	Stonebass (*Polyprion americanus*)	S. Atlantic	27·5	7–18	120–160	65–70	10	120–150	1·6	13–24	110–140	2·8	3–9	155–160
Scombroidæ	Snoek (*Thyrsites Atun*)	S. Atlantic	12	14–19	160–180	81	12	165–175	1·5	8–19	120–160	1·6	8–13	160–170
Gadidæ	Stockfish (*Merluccius Capensis*)	S. Atlantic	16–17	0·3	?	75	0·8	?	3	40–50	140–160	1·0	2·0–3·5	170–195
Ophidiidæ	Kingklip, Cape Ling (*Genypterus Capensis*)	S. Atlantic	18–21	0·2–0·3	?	69–77	0·1	?	2–3	30–40	140–160	2·0	0·7–1·1	?
Triglidæ	Gurnard (*Chelidonichthys Capensis*)	S. Indian	20–25	2–4	?	68–71	1–2		1·0–2·0	8–12	110–140	2·0–2·5	1–4	140–160
Sciœnidæ	Kabeljou (*Sciæna hololepidota*)	S. Indian	16–21	2·2–8·8	160–180	70–78	1–4	147–171	1–1·5	3–20	100–145	1·2–1·5	up to 1	127–167
Sciœnidæ	Geelbek (*Atractoscion æquidens*)	S. Indian	14–18	10–15	165–174	75–77	1–5	168–170	1–3	5–30	125–170	ca.·1	1–2	160–165
Zeidæ	Cape John Dory (*Zeus Capensis*)	S. Atlantic	19–24	0·8–1	160–174	60–66	5–6	153–173	4–5	14–23	140–150	11–18	10–25	140–150

Head, body, liver and viscera oils of some South African marine fish. Rapson, Schwartz and van Rensburg[90a] have published interesting observations on a number of fish from the South Atlantic and southern Indian oceans, in which (as in the groper) head and body tissues appear to be the chief fat depots rather than the liver or mesenterium, the former frequently containing about four times as much fat as the latter. Nevertheless, in these fish, as in others, the liver and body fat stores are more freely metabolised—laid down or withdrawn—than head or visceral fats. In general, as in the groper, the liver fats of this group of fish are almost always less unsaturated than the fats in the main stores (head and body).

Examples illustrating the distribution of fat in these fish, and the mean unsaturation (iodine value) of the various fat deposits are given in Table 14A (p. 53), and detailed component acid figures as observed by van Rensburg[90b] for the various fats from the jacopever are reproduced in Table 14B. It will be seen from the latter table that the component acids of the head, body and intestinal fats are much alike, and that their unsaturated acids are uniformly more unsaturated than the corresponding liver fatty acids; moreover, the general composition of these fats is quite similar to marine fish body fats from the Northern Hemisphere. The liver fat, like those of the stockfish, groper, New Zealand ling, etc., shows lower general unsaturation and the enhanced content of unsaturated C_{18} acids which is evidently characteristic for liver oils of marine fish in the Southern Hemisphere.

TABLE 14B. *COMPONENT ACIDS (WTS. PER CENT.) OF JACOPEVER FATS*

	SATURATED				UNSATURATED					
	C_{14}	C_{16}	C_{18}	C_{20-22}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
Head	2·6	16·3	2·1	0·8	0·9 (−2·0H)	11·8 (−2·0H)	30·3 (−3·0H)	18·8 (−6·8H)	15·5 (−9·6H)	1·0 (−?H)
Body	2·6	13·8	1·8	0·2	2·3 (−2·0H)	12·4 (−2·0H)	28·5 (−2·4H)	21·6 (−7·0H)	16·8 (−9·5H)	— —
Liver	1·2	11·6	3·9	0·4	0·6 (−2·0H)	13·5 (−2·0H)	46·3 (−2·3H)	12·7 (−6·3H)	7·5 (−8·7H)	2·4 (−?H)
Viscera (intestinal)	3·0	14·4	2·2	0·1	1·9 (−2·0H)	13·1 (−2·0H)	30·6 (−2·5H)	19·7 (−6·9H)	12·3 (−9·2H)	2·6 (−?H)

COMPONENT ACIDS OF FATS OF MARINE MAMMALIA

Marine mammals such as the seal, whale, or porpoise possess a layer of fatty tissue beneath the skin, known as blubber, which is the source of considerable quantities of useful technical fatty oils. Certain species such as the sperm whale, dolphin, porpoise, etc., also have deposits of fat in the head cavity, and occasionally in the jaw. Such detailed analyses as are available have usually reference to one or other of these fat deposits; detailed information on the fats of the liver or other organs is for the most part still lacking.

The Seal family (Phocidæ). Seal blubber oil has been used for various purposes for at least as long as whale oil, but no very definite analysis of its component acids appears to have been made until some data were given in 1935 by Williams and Makhrov.[63] These authors suggested that the percentage of the various component acids (wt. per cent.) is somewhat as follows: saturated (mainly palmitic), 18; liquid mono-ethenoid (presumably hexadecenoic and oleic), 61; solid mono-ethenoid (? gadoleic, etc.), 7; and highly unsaturated acids (? C_{20} and C_{22}), 14 per cent. The semi-quantitative analytical data of Tsujimoto[64] and Bauer and Neth[65] support the view that seal oil and ordinary whale oil are similar in fatty acid composition.

A more recent analysis by the ester fractionation method by Burke and Jasperson[86] gives the component acids of Newfoundland seal blubber oil as myristic 5·1, palmitic 10·7, stearic 1·3, arachidic 0·6, unsaturated C_{14} 1·8, unsaturated C_{16} 10·5(−2·1H), unsaturated C_{18} 39·6(−2·4H), unsaturated C_{20} 17·6(−5·6H), unsaturated C_{22} 10·6(−9·3H), and unsaturated C_{24} 2·1 (−10·9H) per cent. (wt.). Compared with, for instance, Antarctic whale oil, the chief differences appear to be less palmitic and hexadecenoic, and somewhat more of unsaturated C_{20} and C_{22} acids.

The Whale family (Balænidæ). In view of the technical importance which whale oil has attained during the past quarter of a century, much study has been given to the general characteristics of the blubber oil. Systematic studies of the effect of various factors on the composition of whale fats have been undertaken by several Scandinavian workers. Lund[56] has summarised the results of records extending over twenty-five years on whale oil from different species, different localities, different parts of the animal, and from fat and lean whales. The latter yield oils of lower iodine values than those from fat whales. The saponification and iodine values of the blubber oils from different species of whales show consistent, if not very large, variations and suggest the influence of variation in the food. Lund's paper contains a very large number of interesting statistics of the analytical characteristics of whale oils from both northern and southern hemispheres, and should be read by all interested in this subject. A similar review of many samples of oil from different parts and different specimens of the blue whale, together with detailed component acid analyses in certain cases, has been published by Tveraaen,[57] whilst corresponding data for the principal food (*Euphausia superba*) of the whale and for the composition of whale milk fat are given by Klem,[7] who also discusses the influence of pregnancy and lactation on the composition of the oil from various parts of the body of the whale.

On the other hand, not many detailed component acid analyses are available in the case of whale oil, these comprising three studies carried out many years ago in the earliest days of the ester-fractionation procedure, and two comparatively recent investigations (Table 15).

TABLE 15. *COMPONENT ACIDS (WTS. PER CENT.) OF WHALE BLUBBER FATS (BALÆNIDÆ)*

	SATURATED			UNSATURATED				
WHALE OIL	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Arctic[58]	4·1	10·6	3·5	—	18·4 (−2·5H)	32·8 (−3H)	19·3 (−7H)	11·3 (−8H)
Newfoundland[58]	7·6	9·7	2·8	1·4 (−2H)	18·3 (−2H)	43·9 (−2·4H)	—	16·0 (−8H)
South Sea[58]	8·0	12·1	2·3	1·5 (−2H)	15·0 (−2H)	42·4 (−2·4H)	8·2 (−7·5H)	10·5 (−9H)
Antarctic[57]	7·6	19·6	—	1·4 (−2H)	11·6 (−2H)	39·1 (−2·9H)	14·7 (−6·8H)	6·0 (−9·6H)
Antarctic[59]	6·3	18·2	2·4	3·7 (−2H)	13·3 (−2H)	38·4 (−2·6H)	11·4 (−5·6H)	6·3 (−9·0H)
Antarctic[87]	9·3*	15·6	2·8	2·5 (−2·0H)	14·4 (−2·1H)	35·2 (−2·5H)	13·6 (−7·2H)	5·9 (−10·1H)

* Also 0·2 per cent. lauric, 0·3 per cent. arachidic, and 0·2 per cent. unsaturated (−10·4H) C_{24} acids.

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It is possible that the figures for the C_{20} and C_{22} acids in the older analyses may be not very accurate—the complete absence of C_{20} acids from the Newfoundland oil is of course very unlikely, in the light of all recent analyses of marine animal fats. Apart from this, however, there can be little doubt that the Arctic whale oils usually contain considerably more highly unsaturated C_{20} or, at all events, C_{22} acids than the oils from Antarctic regions. The iodine values of the latter are invariably lower than those of the former (110–120 for Antarctic as compared with 140–150 for Arctic and Greenland oils). The general characteristics of whale oils from different regions as given by Lund (*loc. cit.*) also illustrate these differences in composition. How far such variations are due to differences in food, in temperature, or in salinity of the sea-water, etc., or to species differences, is not yet clear. No detailed analyses of a comprehensive nature have yet been carried out on the component acids of oils from the various species of whale, but many records have been given by Japanese and other workers of the general analytical characteristics of whale blubber oil from the more common species, such as the Greenland, right, finner, sei, humpbacked, and other whales.

The Antarctic blubber oils have a range of component acids which is, on the one hand, somewhat similar to that of some of the New Zealand fish liver oils (*cf.* Table 4, pp. 36, 37) in the slightly low content of hexadecenoic acid and the high content of unsaturated C_{18} acids (approaching 40 per cent.); on the other hand, there are resemblances to typical English fresh-water fish liver fats in the unsaturated C_{18} acid content and also in the relatively low content of C_{22} acids with a high degree of average unsaturation. The differences are sufficient, however, to justify the Antarctic whale blubber acids being considered, for the present at any rate, as a fairly distinct type of mixture; moreover, the content of saturated acids is high (over 25 per cent.) and the proportion of myristic acid is definitely larger than in the great majority of fish oils. Oleic acid accounts for nearly 90 per cent. of the unsaturated C_{18} acids, the rest being made up of small amounts of octadecatetraenoic acids and octadecadienoic acids, but the ordinary linoleic acid of seed fats is not present in detectable quantities amongst the latter (Green and Hilditch).[42]

The component acids of whale liver oil are of biochemical interest. Klem[7] has given the following figures for the liver oil of a blue Antarctic whale: fatty content of liver, 3·5 per cent.; liver oil, iodine value 166, unsaponifiable matter 9·3 per cent.; fatty acids, mean molecular weight 303, "solid" acids 24 per cent., highly unsaturated acids 18·1 per cent. The fatty acid characteristics suggest close similarity between the component acids of the liver and blubber fats.

It is even more interesting to find that the component acids of whale milk fat are also very similar in type to those of the liver and of the main depot fats. Schmidt-Nielsen and Frog[60] state that, in finner whale milk fat, acids of lower molecular weight than lauric are absent, and that the proportions of the chief homologous series of acids present are C_{14} 5·5, C_{16} 22, C_{18} 32, C_{20} and C_{22} 39 per cent. Since hexadecenoic, oleic, gadoleic, and "clupanodonic" acids were identified and the iodine value of the milk fat was 138·7, it seems almost certain that the composition of the whale milk fat is very little different from that of the blubber fat. Klem[7] has given similar data for the milk fat of a blue Antarctic whale: component acids, saturated, C_{14} 8·4, C_{16} 16·8, C_{18} 1·8 per cent.; unsaturated, C_{14} 1·2 (−2H), C_{16} 6·2 (−2H), C_{18} 26·8 (−3·3H), C_{20} 25·9 (−8·5H), and C_{22} 12·9 (−11H) per cent. It would therefore appear that the characteristic presence of the saturated acids of lower molecular weight (down to butyric acid) is confined to the milk fats of land animals; even here (*cf.* Chapter III, pp. 112, 125–129) the proportions of these lower saturated acids vary quite considerably in different species of mammals.

The sperm whale family (Physeteridæ). The oils from the blubber and the head cavity of the sperm whale (*Physeter macrocephalus*) differ from those of other whales in that they consist mainly of esters (waxes) of higher aliphatic alcohols and acids, with only subordinate amounts of glycerides. Further, their component fatty acids are quite distinct in type from those of ordinary whale oil or of other marine animal oils. Unsaturation is almost wholly confined to the mono-ethenoid state, and the average molecular weight of the acids is lower in both head and blubber oils than in ordinary whale oil. This is illustrated by the detailed analyses of Antarctic sperm whale oils in Table 16 (Hilditch and Lovern).[61]

TABLE 16. *COMPONENT FATTY ACIDS (WTS. PER CENT.) OF SPERM WHALE HEAD AND BLUBBER OILS*

	HEAD OIL	BLUBBER OIL
SATURATED ACIDS :—		
Decanoic	3·5	—
Lauric	16	1
Myristic	14	5
Palmitic	8	6·5
Stearic	2	—
UNSATURATED ACIDS :—		
C_{12} series	4 (−2H)	—
C_{14} "	14 (−2H)	4 (−2H)
C_{16} "	15 (−2H)	26·5 (−2H)
C_{18} "	17 (−2H)	37 (−2H)
C_{20} "	6·5 (−2H)	19 (−2·5H)
C_{22} "	—	1 (−4H)

The blubber oil acids resemble other whale blubber acids much more closely than those of the head oil; but unusually large proportions of hexadecenoic and C_{14} acids, with minor amounts of lauric acid, are present even here, whilst oleic is practically the only unsaturated C_{18} acid and the amount of polyethenoid C_{20} or C_{22} acids is extremely small. The head oil is almost unique (for an animal oil) in its content of decanoic, lauric, and myristic acids, the fat of the amphibian green turtle (Chapter III, p. 69) being the only other similar case at present recorded of the presence of relatively large amounts of lauric and myristic, as well as palmitic, acid. The proportion of oleic acid in the head oil is remarkably small and, although a small percentage of gadoleic acid was observed, C_{22} acids are absent.

The hexadecenoic and oleic acids of both oils have the usual (Δ^9) structure. The unsaturated C_{14} acid of the head oil is Δ^5-tetradecenoic acid (Tsujimoto,[62] Hilditch and Lovern,[61] Toyama and Tsuchiya [63]), and according to the Japanese workers the same acid is present in the blubber oil; Hilditch and Lovern, however, identified a Δ^9-tetradecenoic acid in the latter. Toyama and Tsuchiya [64] also state that the mono-ethenoid C_{12} acid of the head oil is Δ^5-dodecenoic acid and that it is present in traces in the blubber oil; whilst they found traces of a Δ^9-decenoic acid in the head oil.

The sperm head oil studied by Hilditch and Lovern [61] consisted of a mixture of about 74 per cent. of wax esters with 26 per cent. of triglycerides, whilst the blubber oil contained about 66 per cent. of wax esters and 34 per cent. of triglycerides. The proportions of the chief component alcohols were approximately as follows :—

	HEAD OIL	BLUBBER OIL
SATURATED ALCOHOLS :		
C_{14} Tetradecyl	8	—
C_{16} Hexadecyl (cetyl)	44	25
C_{18} Octadecyl	6	1
UNSATURATED ALCOHOLS :		
C_{16} Hexadecenyl	4	—
C_{18} Octadecenyl (oleyl)	28	66
C_{20} Eicosenyl	10	8

(Weitkamp and Brunstrum [88] have also determined the components of "sperm oil alcohols"—apparently from sperm blubber oil—by ester fractionation and record the following data : saturated alcohols, C_{14} 2·1, C_{16} 21·1, C_{18} 5·0 ; mono-ethenoid unsaturated alcohols, C_{14} trace, C_{16} 7·4, C_{18} 49·7, C_{20} 6·1 ; and di-ethenoid unsaturated C_{20} alcohols 2·1 per cent. (weight).)

The head oil contained nearly 30 per cent. of fully saturated esters and glycerides ; the component acids present as glycerides or wax esters in the fully saturated portion were made up of decanoic 13·5, lauric 41·5, myristic 29, palmitic 12, and stearic 4 per cent. ; whilst the corresponding alcohols consisted of tetradecyl 13, hexadecyl 80, and octadecyl 7 per cent. Thus there is a distinct tendency for the fully saturated wax esters to be formed preferentially from the acids and alcohols of lower, rather than from those of higher, molecular weight. The chief constituents of "spermaceti," accordingly, will tend to be cetyl myristate and laurate, rather than cetyl palmitate. Hilditch and Lovern [61] were able to give a rough outline of the probable main classes of esters and glycerides (saturated, saturated-unsaturated, and wholly unsaturated) present in the sperm head oil (*cf.* original, *loc. cit.*).

The blubber oil contained only about 2 per cent. of fully saturated esters or glycerides and no detailed statement of its structure could be given. The main components are evidently oleyl oleate and oleyl hexadecenoate with subordinate proportions of cetyl oleate and hexadecenoate, together with the 34 per cent. of mixed triglycerides of the component acids.

The segregation of the acids and alcohols of lowest molecular weight in the head oil, and also of these components into the fully saturated portions of the latter, is a phenomenon similar to that observed subsequently in a number of other instances. It is an example of the behaviour which Lovern has correlated with a possible "filtration" or "absorption" mechanism in which molecular size is considered to operate as a controlling factor in the type of fat deposited.

Other alcohols than those mentioned as chief components have been detected in small amounts in the sperm oils. These include Δ^5-tetradecenyl alcohol in the head oil (Toyama and Tsuchiya [65]), and traces of Δ^9-hexadecenyl alcohol, of an eicosatetraenol, $C_{20}H_{33}.OH$, and of a docosapentaenol, $C_{22}H_{35}.OH$ (Toyama and Akiyama [66]).

It is of the greatest interest to note that the liver oil of the sperm whale is apparently largely glyceridic and that its component acids align themselves with other marine animal liver oils. Tsujimoto and Kimura [67] have given a partial analysis of the mixed acids of sperm whale liver oil as follows: saturated acids (chiefly palmitic) 25, mono-ethenoid acids 42, and poly-ethenoid (C_{20} and C_{22}) acids 23 per cent. This composition is clearly similar to that of the majority of marine fish liver acids. The characteristic alcohols, and lower fatty acids, of the sperm whale depot fats are therefore substantially absent from the liver fat. The same circumstances occur also in the case of dolphin and porpoise fats (*cf.* below).

Although the most familiar instance of the occurrence in large amounts of wax esters in an animal fat, the sperm head and body oils must not be supposed to be unique in this respect. There may well be other examples so far unobserved. Indeed, Tsujimoto [68] has recently stated that the fat of the ovary of the grey mullet (*Mugil Japonicus*) contains 40 per cent. of " unsaponifiable matter," which is made up (apart from about 9 per cent. of cholesterol) of a mixture of cetyl, octadecyl, hexadecenyl, and oleyl alcohols; the fatty acids, with an iodine value of 186, yielded over 50 per cent. of ether-insoluble bromo-additive products and therefore (in the absence of any more detailed analysis) would appear to belong to one or other of the " aquatic " types of fatty acid mixtures. The original " fat," so far as can be judged from the merely qualitative data given, certainly contained a high proportion of wax esters and was apparently not very dissimilar from sperm blubber oil.

The dolphin and porpoise family (Delphinidæ). In this group we encounter the most extreme case of an anomalous depot fatty acid, namely, the occurrence in quantity of the branched-chain, " odd-number," *iso*valeric acid, $C_5H_{10}O_2$, in the jaw, head, and blubber fats of this family of marine mammals. The acid was actually first observed in dolphin oil by Chevreul,[69] although it was not until comparatively recently that its identity as *iso*valeric acid, $(CH_3)_2CH.CH_2.COOH$, was definitely confirmed (Gill and Tucker [70]; Klein and Stigol [71]). Gill and Tucker [70] found in the jaw oil of a species of dolphin (*Tursiops truncatus*) 86·7 per cent. *iso*valeric, 8·4 per cent. palmitic, and 4·9 per cent. oleic acid; the oil contained about 19 per cent. of higher fatty alcohols in addition to glycerides.

The most complete information yet available for these fats is, however, the detailed analysis by Lovern [50] of the body and head oils of a dolphin (of unknown species), together with similar studies of the body, head, jaw, and various organ fats of an adult female porpoise (*Phocæna communis*) with a well-developed fœtus. Some particulars of these different fats are given in Table 17.

TABLE 17. *PARTICULARS OF DOLPHIN AND PORPOISE FATS (LOVERN [50])*

SPECIES	FAT FROM	FAT IN TISSUE (Per Cent.)	IODINE VALUE	SAP. EQUIV.	UNSAPONIFIABLE	
					(Per Cent.)	Type
Dolphin	Body blubber	80–90	136·0	263·4	2·2	Mainly higher alcohols.
"	Head blubber	80–90	82·33	228·4	7·5	" "
Phocæna communis	Body blubber	80–90	88·82	225·7	2·4	" "
" "	Head blubber	80–90	64·76	204·7	2·1	" "
" "	Jaw	80–90	44·93	196·3	3·6	" "
" "	Fœtal body blubber.	80–90	108·9	267·8	2·4	Largely cholesterol
" "	Heart	ca. 2	121·3	—	9·7	Mainly cholesterol
" "	Lungs	ca. 2	119·5	—	15·0	" "
" "	Liver	ca. 5	175·0	—	32·1	" "

The weight and molar percentages of the component acids in each fat of Table 17 are given in Table 18; owing to the extreme difference in molecular size between *iso*valeric and, for example, C_{22} acids it becomes urgent here to make comparisons on a molar, and not merely a weight, percentage basis.

TABLE 18. *COMPONENT ACIDS OF DOLPHIN AND PORPOISE FATS (LOVERN*[50]*)*

(i) *Weight Percentages*

SPECIES	DEPOT	SATURATED					UNSATURATED				
		C_{5}	C_{12}	C_{14}	C_{16}	C_{18}	C_{14}†	C_{16}†	C_{18}	C_{20}	C_{22}
Dolphin	Body	3·2	1·0	7·2	8·6	0·8	4·7	25·9	24·1 (−3·3H)	18·6 (−6·5H)	5·9 (−7·6H)
,,	Head	13·9	2·4	12·5	11·6	0·4	2·7	25·4	15·8 (−2·8H)	12·7 (−5·5H)	2·6 (−7·2H)
Phocæna communis	Body	13·6	3·5*	12·1	4·7	—	4·7	27·2	16·7 (−2·8H)	10·5 (−4·8H)	7·0 (−4·9H)
,,	Head	20·8	4·1	15·8	7·5	0·2	4·6	20·8	15·2 (−2·6H)	9·4 (−4·5H)	1·6 (−4·7H)
,,	Jaw	25·3	4·6*	28·3	4·1	—	3·2	20·3	9·3 (−2·6H)	4·9 (−4·9H)	—
,,	Fœtus	1·2	—	14·9	0·6	—	12·3	48·1	15·4 (−4·0H)	7·5 (−7·4H)	—
,,	Liver	—	—	—	7·6	5·5	—	6·1	42·5 (−2·8H)	27·3 (−5·4H)	11·0 (−6·5H)
,,	Lungs	—	—	4·6	9·0	1·2	0·1	16·5	27·0 (−2·4H)	31·0 (−3·3H)	10·6 (−5·4H)
,,	Heart	—	—	8·1	8·2	4·4	4·4	16·8	50·4 (−3·6H)	7·6 (−5·4H)	—

(ii) *Molar Percentages*

SPECIES	DEPOT	SATURATED					UNSATURATED				
		C_{5}	C_{12}	C_{14}	C_{16}	C_{18}	C_{14}†	C_{16}†	C_{18}	C_{20}	C_{22}
Dolphin	Body	8·0	1·3	8·1	8·6	0·7	5·3	26·1	21·9	15·5	4·5
,,	Head	29·2	2·6	11·7	9·7	0·3	2·5	21·4	12·0	8·9	1·7
Phocæna communis	Body	28·7	3·8	11·4	3·9	—	4·5	23·0	12·8	7·4	4·5
,,	Head	39·6	4·0	13·4	5·7	0·1	3·9	16·0	10·5	5·9	0·9
,,	Jaw	44·7	4·1	22·4	2·9	—	2·6	14·4	6·0	2·9	—
,,	Fœtus	2·9	—	16·2	0·6	—	13·5	47·0	13·7	6·1	—
,,	Liver	—	—	—	8·6	5·6	—	6·9	43·7	25·7	9·5
,,	Lungs	—	—	5·7	10·0	1·2	0·1	18·4	27·2	28·4	9·0
,,	Heart	—	—	9·5	8·6	4·2	5·2	17·7	48·2	6·6	—

* Trace of dodecenoic acid present.

† The unsaturated C_{14} and C_{16} acids were substantially mono-ethenoid.

Perhaps the most remarkable feature of the figures in Table 18 is that the porpoise organ fats, without exception, contain no *iso*valeric and lauric acids, and do not contain unusually large proportions of C_{14} and C_{16} acids. High proportions of the acids of low molecular weight, and the presence of *iso*valeric acid, are confined to the depot fats of the body, head, and jaw of the animal. The fœtal fat had only a minute amount of *iso*valeric acid, but contained large quantities of C_{14} and C_{16} acids, whilst the degree of unsaturation of the C_{18} and C_{20} acids was the highest in the whole series, considerably higher even than that of the maternal liver. It appears that *iso*valeric acid was not passed through the placenta, and that the portion found in the fœtal blubber was produced by metabolic processes in the fœtus itself. A small amount of fat was isolated from the placenta and the glyceride and phosphatide fractions separated. No *iso*valeric acid was present, and the glyceride acids had an iodine value of 117·7 and a mean equivalent of 275·5. Hence no large proportions of C_{14} and C_{16} acids could have been present.

Further, Lovern studied the glyceride structure of the porpoise body fat and proved that four-fifths of the *iso*valeric acid present was in combination with higher fatty acids in the form of mixed saturated-unsaturated glycerides, whilst the remaining fifth was present in mixed fully saturated glycerides, but no tri-*iso*valerin was detected. Hence, although *iso*valeric acid is absent from the liver or other organ fats, its mode of association in the depot fat glycerides with the higher fatty acids is exactly similar to the manner in which the latter are themselves assembled as mixed glycerides. The lower normal fatty acids (C_{12}, C_{14}) are, as in other cases, concentrated in the fully saturated glycerides in preference to palmitic or stearic acids, but this does not hold to any extent in the case of *iso*valeric acid.

Lovern has pointed out a progressive change in the total amounts of the different molecular groups present in the body, head, and jaw depot fats. For instance, in *Phocæna communis*, on passing from body to head and head to jaw, the *iso*valeric, lauric, and myristic acid contents rise steadily, and the C_{18}, C_{20}, and C_{22} acids fall. This is shown by the molar percentages of each homologous group of acids given in Table 19.

TABLE 19. *ACIDS OF DOLPHIN AND PORPOISE DEPOT FATS ARRANGED IN MOLECULAR GROUPS*

SPECIES	DEPOT	C_5	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Dolphin	Body	8·0	1·3	13·4	34·7	22·6	15·5	4·5
,,	Head	29·2	2·6	14·2	31·1	12·3	8·9	1·7
Phocæna communis	Body	28·7	3·8	15·9	26·9	12·8	7·4	4·5
,,	Head	39·6	4·0	17·3	21·7	10·6	5·9	0·9
,,	Jaw	44·7	4·1	25·0	17·3	6·0	2·9	—

This description of the dolphin and porpoise fats may be concluded with some quotations from Lovern's discussion (*loc. cit.*) of the question :

> "This suggests that one of the mechanisms operating in the case of these animals to control the type of fat laid down in the different depots rests on a basis of molecular size and might almost be some form of molecular filtration. Presumably the acids enter the depots as glycerides and not as free fatty acids, but in either case similar reasoning could be applied. If we visualise fat deposition taking place selectively on any basis of permeability differences, we should expect to find, *mutatis mutandis*, that the less permeable depots (as found by analysis of the fatty acids) would be the smaller in size. Low molecular weight components will find equally easy entry into all depots, but the larger molecules will only readily enter the more permeable depots. In actual fact, such is the case. In the dolphin and porpoise, the body fat is much greater in quantity than the head fat, which in turn is much greater than the jaw fat.
>
> "The peculiar composition of the porpoise and dolphin depot fats raises some interesting questions. Where, for instance, is the site of the production of the lower fatty acids, due perhaps to breakdown of the C_{20} and C_{22} acids ? Also of the *iso*valeric acid, which is apparently produced quite separately, and combined into mixed glycerides in a different manner from the other lower acids ? That this site is the liver seems most unlikely, in view of the apparent entire absence of these acids from it—indeed, the liver fat closely resembles the other organ fats

examined. In fact, the organ and the depot fats are so thoroughly different in their whole composition that it is difficult to imagine the liver playing any large part in the metabolism of these depot fats. An organ that is worthy of attention in this respect is the spleen, in view of its function of removing fat from the blood during alimentary lipæmia (Marino [72]), and hence its role as an intermediary in the formation of depot fats from food fat (*cf.* also Leites *et al.*[73]).

"In the case of the fœtus it seems probable that the fat received from the maternal system is mainly of the ordinary marine type. This is modified by the fœtus in two ways: by production of much C_{14} and C_{16} acids in place of C_{20} and C_{22}, and by admixture of *iso*valeric acid. The metabolic process from which the *iso*valeric acid arises evidently does not function to any great extent up to this stage. The characteristic composition of the fœtal fat is further evidence that the *iso*valeric acid and the lower *n*-acids are produced by separate processes."

Another series of analyses of body, head, and jaw fatty acids from a further member of this family of marine mammals (the "white whale," *Delphinapterus leucas*) has since been published by Williams and Maslov,[74] who give the data reproduced in Table 20.

TABLE 20. *COMPONENT ACIDS (WTS. PER CENT.) OF DEPOT FATS OF DELPHINAPTERUS LEUCAS*

ACID	BODY (Per Cent.)	HEAD (Per Cent.)	JAW (Per Cent.)
*Iso*valeric	4·0	25·1	20·0
Palmitic and Stearic	28·0	29·1	14·1
Hexadecenoic	—	30·2	—
Oleic	51·0	—	50·4
Linolenic	0·1	0·7	1·2
Stearidonic	—	0·3	—
"Clupanodonic"	1·2	0·6	1·4

Apart from obvious deficiencies in these figures, they show a somewhat similar character to those for the dolphin and porpoise in so far as the *iso*valeric acid contents are concerned.

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CHAPTER III

THE COMPONENT ACIDS OF FATS OF LAND ANIMALS

FATS occur in many different parts of animals, as they do in plants (*cf.* Chapter IV). In each division, vegetable or animal, they are found both in the organs and tissues concerned with the growth and maintenance of life, and in special locations or depots (fruits in the vegetable world and adipose tissues in the animal kingdom) where they are stored as reserve material. Further, a special type of fat is usually present in the milk secreted by mammals as food for their young.

Discussion of the ultimate composition of these various groups of animal fats is subject to the usual limitations, namely, paucity of detailed fatty acid analyses in spite of abundant data on saponification values, iodine values, etc.,* of individual fats or of their corresponding " mixed fatty acids." As has happened in the vegetable fats, the land animal depot fats hitherto studied in detail are those which are most common, most readily obtained in quantity in a pure state, and, incidentally, most in demand for edible or other industrial purposes. There is a consequent lack of perspective in any detailed description of the fatty acids of land animals as a whole, because attention has hitherto been focussed far too much on relatively few species. There are, for example, hardly any detailed data available for depot fats of the Carnivora, and almost none for those of the Primates (including human fat). Indeed, owing to the work carried out on fats of aquatic animals during the past few years, knowledge of the component fatty acids in the latter group is at present far more comprehensive than of land animal depot fats; although, as stressed in the previous chapter, the instances there available still form an unduly small proportion of the whole range of natural fats of aquatic fauna. On the other hand, owing to the comparative simplicity of the major components (palmitic, stearic, oleic, and polyethenoid C_{18} acids) present in the majority of the depot fats of, at any rate, the larger land animals, it is to some extent permissible, although not altogether safe or desirable, to use the average molecular weights and iodine values of the mixed fatty acids (especially if the proportions of " solid " and " liquid " acids have been recorded) as an indication of the probable composition of some of the depot fats for which no more detailed information has so far been given.

It is only possible, consequently, at the present time to give an account of the animal depot fats of which the component acids have been adequately studied, to supplement this to some extent, and with discretion, from the general or average data on record in other instances, and to indicate the lacunæ which remain to be filled by future experimental work.

The constitution of the fats (glyceridic and phosphatidic) of animal organs has been investigated in still less detail than that of the depot fats, owing doubtless to the smaller proportions of fatty matter usually present in most organs as compared with adipose tissue, and to the difficulties of separating organ fats in a pure condition in sufficient quantity for full examination. The same statement applies to milk fats, although during the last few years several welcome detailed analyses have appeared on the component acids of the milk fats of a number of different species of animals.

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* Not to mention specific gravities or refractive indices, which are usually faithfully recorded, but which unfortunately do not assist in defining the quantitative composition of the fatty acids present !

In this chapter we shall consider in succession, and subject to the limitations already mentioned, the chief features of the component acids of land animal depot, organ (mainly liver) and milk fats.

Component Acids of Depot Fats (Glycerides) of Land Animals

In discussing the available data for the depot fats of the different categories of land animals, attention will be directed primarily to fats from animals whose diet has not contained more than two or three per cent. of fat, such fat being, as it were, that present in the normal food of the species (grass, grain, etc., as the case may be). When animals are fed on rations containing relatively large proportions of fat, much of the dietary fat may be more or less directly assimilated and the composition of the resulting depot fats is affected to a considerable extent according to the nature and amount of the fat ingested by the animal. This will be illustrated subsequently by examples in which animals have been fed on a high fat ration of known composition, and their depot fats submitted to detailed examination.

It should be pointed out here that animal adipose tissue fats consist, as a rule, almost wholly of glycerides. In liver and other organ fats, in contrast, it is usual to find that the fatty matter also contains fairly large proportions of phosphatides, and also cholesterol and/or cholesterol fatty esters, in addition to mixed triglycerides.

INVERTEBRATA

Before proceeding to discuss the depot fats of vertebrate land animals, the existing information on fats of invertebrate land animals (very slight in amount, and nearly all concerning insects) may receive brief notice.

Although the components of a few fats of marine invertebrates have been determined (Chap. II, pp. 24–29), the only detailed study of a fat of a land invertebrate (other than insects) appears to be an account by Lovern[1] of the fatty matter which is present to the amount of 1·2–1·3 per cent. in the common earthworm (Lumbricidæ). Of the total lipids, 56–67 per cent. were glyceridic, and 44–33 per cent. phosphatidic, in character; but each group contained over 50 per cent. of unsaponifiable or non-fatty matter. Both groups contained unknown acids in addition to fatty acids of the C_{10}–C_{22} series; Lovern gives the following provisional analysis of the component acids of the glyceride and phosphatide fractions:

SATURATED ACIDS

	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	over C_{18}
Glyceridic	1	4	6	6	13	2
Phosphatidic	—	3	2	5	8	3

	UNSATURATED ACIDS						
	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	over C_{22}
Glyceridic	3 (−2·0H)	4 (−2·9H)	3 (−2·8H)	22 (−4·2H)	26 (−6·5H)	2 (−?H)	8 (−?H)
Phosphatidic	1 (−2·0H)	1 (−2·0H)	?	4 (−3·7H)	42 (−4·7H)	17 (−4·4H)	14 (−?H)

The very low hexadecenoic acid contents, and the preponderance of stearic over palmitic acid, appear noteworthy.

INSECT FATS

"Chrysalis oil," which forms about 25 per cent. of the cocoon of the silkworm, *Bombyx mori*, has received most attention. Kimura [2] gave the fatty acid composition as about 25 per cent. of saturated (mainly palmitic) acids with about 22 per cent. oleic, about 38 per cent. linoleic and about 15 per cent. linolenic acids, whilst a recent communication by Bergmann [3] states that the average composition is: palmitic 20, stearic 4, arachidic, etc., less than 1; hexadecenoic 2, oleic 35, linoleic 12, linolenic 25 and higher unsaturated acids 1–2 per cent. Bergmann [3] adds that the chrysalis fat of the tent moth, *Malacosoma americana*, has a similar composition. Bachstez and Aragon [4a] have determined the component acids of the fat of the caterpillar of *Acentrocneme hesperiaris* which feeds on the leaves of the Mexican agave, the sap of which contains cane sugar and invert sugar. These larvæ are eaten in Mexico as a delicacy after frying in their own fat (which forms about 35 per cent. of the dry weight of the caterpillar). The fat, which in this instance is almost certainly synthesised by the insect from sugar, contained as component acids palmitic 30·6, stearic 3·7, oleic 61·3, and linoleic 4·4 per cent. (wt.). Hastings and Pepper [4b] have recorded that the larval fat of the diapausing codlin moth (*Carpocapsa pomonella*) contains as component acids saturated 3·6, oleic 75·3, and linoleic 21·1 per cent. (wt.).

Of insect body fats, locust (*Oxya japonica*), according to Tsujimoto,[5] contains about 3 per cent. of fat composed of a mixture of about 25 per cent. saturated (palmitic and stearic) and 75 per cent. oleic, linoleic, and linolenic acids; he also states [5] that the 2·4 per cent. of fat in Japanese crickets (*Aceta mitrata*) contains mainly oleic with some polyethenoid C_{18} acids and some saturated acids. The body of a Brazilian butterfly, *Myelobia smerintha*, is stated by Thoms [6a] to contain 22 per cent. of fat, the acids of which consist of about one-third saturated (palmitic and stearic) and two-thirds unsaturated (oleic). J. F. and M. L. Giral [6b] have reported the component acids of the body fats of male and female specimens of *Tæniopoda auricornis* to be: male, saturated 15·5, oleic 24·0, linoleic 60·5; and female, saturated 35·0, oleic 6·5, and linoleic 58·5 per cent. (wt.). The general characteristics of a few other fats of insects belonging to the Coleoptera, Diptera, and Orthoptera have been reported, from which it appears that the major components are oleic and linoleic acids and that, although palmitic acid is probably also present, acids of lower molecular weight are absent. An exception to this statement is, however, found in the fat of *Pemphigus* species (Aphidæ), the acids of which are reported by Schultz [7] to have a mean molecular weight of 218 and to include butyric, caprylic, and lauric as well as palmitic acids.

The body fat of the cantharides beetle has received some attention. Iyer and Ayyar [8] state that fat (including 5 per cent. of unsaponifiable matter) amounts to 12·5 per cent. of the dry weight of the Indian species *Mylabris pustulata*, the component acids being palmitic 13, stearic 32, arachidic 1, and oleic acid 54 per cent. Janot and Faudemay[9] found the proportions of the fatty acids in the lipids of the species *Lytta vesicatoria* to be somewhat variable, the major components being palmitic and oleic acids, with minor amounts of stearic, linoleic, and linolenic acids.

The larvæ of a beetle (*Pachymerus dactris*) which had fed on the endosperm of the nuts of *Manicaria saccifera* (Palmæ) were found by Collin[10] to contain nearly 50 per cent. of fat, the component acids of which were made up approximately as follows: lauric 24, myristic 21, palmitic 8, oleic 32, linoleic 3, and a further 12 per cent. of stearic, oleic, or linoleic acids. Comparing these figures with those for the kernel fat of *Manicaria saccifera* (Chapter IV, p. 200), it appears that the acids of lower molecular weight (of which lauric acid is the chief) are present in the larva fat in only about half the amount in which they occur in the kernel fat, while oleic and linoleic acids probably form about 40 per cent. of the mixed acids in the larva fat, as compared with only 11 per cent. in the kernel fat. This rather suggests that the insect has derived its fat partly by direct assimilation of the preformed vegetable fat, and partly by synthesis from carbohydrate (or other non-fatty) components of the kernel. If this be the case, it would appear that the development of fat in insects may follow a course not very different from that which takes place in the larger land vertebrates.

On the whole, it seems likely that insects, in the larval as well as mature state, lay down fats very similar in type to those produced by mammals, and that, like the latter, they can assimilate fats present in their diet and also synthesise fat from other constituents of the food. More complete study of insect fats than has hitherto been made might well be of interest from a biochemical standpoint.

It will be noted, of course, that here we are considering the glyceridic fat present in insects or their larvæ, and not the waxes elaborated by some species such as, for example, bees or the cochineal insect. Insect waxes consist almost wholly of ester-waxes derived from aliphatic acids and alcohols of higher molecular weight (e.g. C_{26} and upwards) than those present in natural fats. Bees wax, however, is reputed to contain, amongst its acidic components, a certain amount of palmitic acid and small proportions of oleic acid.

VERTEBRATA

DEPOT FATS OF AMPHIBIA AND REPTILES

A few, very significant, detailed investigations of depot fats of the frog, lizard, and turtle family have recently (1933 and subsequently) been made.* Their significance lies in the circumstance that in all cases the component fatty acids form a link intermediate in almost all respects between those of depot fats of aquatic and of land animals. The data in question are collected in Table 21.

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* Previous to these detailed analyses Tsujimoto[11] had noted in 1920 that the fatty acids of many amphibians and reptiles yielded varying proportions of ether-insoluble bromo-additive products which indicated the presence of highly unsaturated acids of the C_{20} and C_{22} series and thus pointed to resemblance to the oils of aquatic fauna. The yields of the bromo-additive products obtained from the mixed fatty acids of different fats were as follows: giant salamander, 21 per cent.; toad, 1 per cent.; turtle, 5 per cent.; red turtle, 31 per cent.; leather turtle, 38 per cent.; giant lizard, 10 per cent.; python, 2 per cent.; viper, 8 per cent.

TABLE 21. *COMPONENT FATTY ACIDS (WTS. PER CENT.) OF AMPHIBIAN AND REPTILE DEPOT FATS*

	SATURATED				UNSATURATED			
	C_{12}	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20-22}
Frog (*Rana temporaria*) [12a]	—	4	11	3	—	15 (−2H)	52 (ca. −2·5H)	15 (ca. −6H)
Lizard (1) (*Varanus salvator*) [12b]	—	4	18	7	—	10 (−2H)	56 (−2·4H)	5 (ca. −5H)
Lizard (2) *Varanus salvator*) [13]	—	4	29	10	—	12 (−2H)	40 (−2·7H)	5 (−5·5H)
Greek tortoise (*Testudo græca*) [12b]	—	1	14	4	—	9 (−2H)	65 (−2·4H)	7 (ca. −4H)
Green turtle (*Chelone mydas*) [14]	13·3*	10·6	17·0	4·1	1·3 (−2H)	7·8 (−2H)	39·6 (−2·2H)	6·1 (−6·3H)
,, ,, (Japan[16])	14·2§	7·2	15·2	6·8	2·6 (−2H)	10·9 (−2H)	39·4 (−2H)	Small (−?H)

* Also 0·2 per cent. decanoic acid.

§ Also 3·5 per cent. hexoic acid ; C_{20-22} acids highly unsaturated.

Despite marked differences in quantitative (and in one case qualitative) composition, it will be seen at once that the unsaturated C_{16} and C_{20-22} acids of the fats in Table 21 are present in smaller proportions than in fish depot fats, whilst the unsaturated C_{18} acids (in which oleic predominates) become the most prominent individual group. We shall find (*vide infra*) that in depot fats of the larger animals the hexadecenoic and C_{20-22} acid contents are reduced to very small proportions. The saturated acids of the fats in Table 21 are more reminiscent of typical fish, etc., fats than the unsaturated components, but in one case the proportion of palmitic acid has risen to the amount characteristic of the larger land animal depot fats.

The data for the fats of the frog, Greek tortoise, and one of the lizards (1) were given in 1933 and 1935 by Klenk, who commented on the circumstance that the fatty acid compositions were intermediate in character between those of corresponding fats from land mammals and fishes. Actually, the frog fat is nearer in type to aquatic than to land animal fats, whilst the Greek tortoise and lizard (1) fats are more definitely intermediate in composition. Of the two lizards, the specimen (1) examined by Klenk was a mature animal which had been kept in captivity for some years, whilst lizard (2), of the same species, was a very young wild animal killed in Ceylon. Differences in diet and other factors may have contributed to the differences (mainly in palmitic and unsaturated C_{18} acid contents) observed in the depot fat component acids.

The fat of the green turtle [14] (a specimen from the Seychelles) stands apart from the rest, since its acids include about 15 per cent. each of lauric and myristic acids. The presence of unusually large amounts of myristic acid in Japanese green turtle fat had been reported by Tsujimoto [15] shortly before the data in Table 21 were given by Green and Hilditch ; Tsujimoto also mentioned the probable presence of lauric and hexadecenoic acids. In the specimen of fat examined quantitatively, lauric, myristic, and palmitic acids occurred in approximately equimolecular proportions and together amounted to half of the total fatty acids. The unsaturated acids conformed with those of the other fats in Table 21, and consisted largely of oleic, with minor proportions of unsaturated C_{16} and C_{20-22} acids. The unusual presence of lauric and the unusually high content of myristic acid in the fat of the green turtle may well be a species distinction ; at all events there would seem to be no likelihood that the normal food of the animal contains fats rich in lauric acid. Hata [17] has described the body fat which forms 1·6 per cent. of another species of green turtle, *C. japonica*, and qualitatively identified a similar range of unsaturated acids to those given in Table 21. He has also stated that the chief component acids of body, liver and ovary fats of the Chinese turtle, *Ocadia sinensis*, are myristic, palmitic, stearic, hexadecenoic and oleic acids ; here the occurrence of lauric acid is not mentioned.

BIRD DEPOT FATS

Birds deposit fat chiefly in the region of the gizzard, which contains an adherent layer of fat, close to the mesenteric membrane. Fat is also present in the mesenteric membrane, and around the kidneys ; whilst there is a fair quantity of adipose tissue in the superficial layers of the abdomen, with other minor deposits of subcutaneous fat in the neck and other parts of the skin.

There are very few detailed analyses of bird depot fats, only those of the domestic hen, grey goose, and emu having been studied by the ester-fractionation process. Goose and hen fats have been partially examined by means of lead salt (Twitchell) or oxidation (Bertram) processes by Bömer and Merten,[18] and by Grossfeld,[19] with the results given below (Table 22) ; apart from this, only general characteristics have been given for a few other bird fats.

TABLE 22. ***COMPONENT ACIDS (WTS. PER CENT.) OF GOOSE AND HEN DEPOT FATS***

(Separation into " solid " and " liquid " acids only.)

	GOOSE FAT		HEN FAT	
	(BÖMER AND MERTEN [18])	(GROSSFELD [19])	(GROSSFELD [19])	
Palmitic	21·8	20·9	18·4	19·3
Stearic	3·9	10·6	8·9	7·5
Oleic	74·3	49·0	54·7	55·4
Linoleic	—	19·3	17·9	17·8

Grossfeld pointed out that the percentage of palmitic acid, calculated from the saponification value of the total mixed fatty acids, was about 10 units higher than that calculated from the molecular weight of the separated " solid " fatty acids, and attributed this to the presence of fatty acids lower in molecular weight than palmitic acid. Hilditch, Jones, and Rhead [20] investigated, by the ester-fractionation procedure, the abdominal, gizzard, and neck fats from two groups of Light Sussex hens (respectively seven months and two years old) which had been reared at the Cambridge School of Agriculture on controlled diets. The results showed that either, as Grossfeld supposed, saturated acids of lower molecular weight than palmitic acid were present or, alternatively, that an unsaturated acid of lower molecular weight than oleic acid was present. Examination of the lower-boiling " liquid " or unsaturated ester fractions did not reveal any saturated acid other than palmitic, but quantitative oxidation with permanganate in acetone clearly indicated that the mean molecular weight of the unsaturated esters was lower than that of methyl oleate. Hydrogenation of the "liquid" esters, followed by fractionation, disclosed a corresponding increase in palmitic esters in the now saturated esters (showing the original presence of a hexadecenoic ester); and independent calculations from the results of the quantitative oxidation and hydrogenation studies gave accordant results for the proportion of hexadecenoic acid present. Finally, the hexadecenoic ester was prepared in a relatively pure condition from a large quantity of the hen fat, and was shown to be the Δ^9-hexadecenoic acid which is a common constituent of aquatic animal fats (*cf.* Chapter II, p. 30). Small amounts of unsaturated acids of the C_{20} and C_{22} series were also detected, and the final results given for the component acids of the six fats are shown in Table 23.

TABLE 23. *COMPONENT FATTY ACIDS (WTS. PER CENT.) OF BODY FATS FROM LIGHT SUSSEX HENS*

	Birds aged 7 Months			Birds aged 2 Years		
	Abdominal	Gizzard	Neck	Abdominal	Gizzard	Neck
Myristic	0·1	0·1	0·3	1·2	0·6	1·2
Palmitic	25·6	25·2	26·7	24·0	25·4	24·5
Stearic	7·0	7·1	5·9	4·1	4·2	4·2
Hexadecenoic	7·0	7·6	6·6	6·7	7·1	6·9
Oleic	38·4	36·9	39·0	42·5	43·0	42·8
Linoleic	21·3	22·8	21·2	20·8	18·4	20·4
C_{20-22} unsaturated	0·6	0·3	0·3	0·7	1·3	Trace

All these fats are closely similar in composition. The resemblance, in this case, between the fats from different parts of the birds presents a marked contrast to the differences found in fats from different depots of some of the larger animals (*cf.* pp. 86, 89, 90, 105). The following features may be emphasised:—

(*a*) Palmitic (with myristic) acid forms 27–28 per cent. (molar) of the total fatty acids; oleic and linoleic acids account for 58–60 per cent. (molar) of the whole. The amount of stearic acid is small (4–6 mols. per cent.).

(*b*) The occurrence of about 7 per cent. of Δ^9-hexadecenoic acid.

(*c*) There are small but definite amounts of highly unsaturated acids of the C_{20} and C_{22} series present, as in the fats of the land mammals.

(*d*) The component acids of the hen fats are much more closely related to such fats as those of the rodents than to those of aquatic fauna, or even of the amphibia or reptiles.

Values obtained in 1943 by Nutter *et al.*[25] for the depot fatty acids of females of four breeds of chickens and of turkeys (*Meleagris gallopavo*) fed on standard rations of mash and grain, are given below. The data are based only on the iodine and thiocyanogen values of the fats, and have been recalculated on the basis of the thiocyanogen values for linoleic acid at present accepted (*cf.* Chapter IV, pp. 138, 139).

	Component Acids (wts. per cent.)		
	Saturated	Oleic	Linoleic
Chicken, New Hampshire Red	26	42	32
,, White Wyandotte	32	38	30
,, Rhode Island Red	26	50	24
,, White Plymouth Rock	25	49	26
Turkey, White Holland	31	43	26
,, Narragansett	25	49	26
,, Bronze	30	47	23
,, Bourbon Red	33	38	29

An ester-fractionation analysis of the component acids of the abdominal fat of a grey lag goose (*Anser anser*, considered to be the immediate wild ancestor of the domestic goose) is recorded by Hilditch and Sime.[21] The bird had been reared in captivity in Colombo, and the chance of its diet having included coconuts or coconut oil cake cannot be excluded. The component acids were found to be lauric 12·3, myristic 8·2, palmitic 20·3, stearic 5·6, tetradecenoic 0·6, hexadecenoic 2·5, oleic 41·6, octadecadienoic 6·6 and highly unsaturated C_{20-22} acids 2·3 per cent. (wt.). The content of hexadecenoic acid resembled that of land mammalian depot fats rather than that of the hen, and although the percentage of palmitic acid is not greatly lower than that of the hen, the presence of relatively large amounts of lauric and myristic acids marks a difference from the latter. Meanwhile, a determination of the component acids of the fat of the domestic goose must be awaited in order to decide whether these lower saturated acids are specific in goose fat or, in the present instance, result from assimilated dietary fat.

The component acids of the subcutaneous fat of an Australian emu (*Dromalus novæ-hollandiæ*), which had also lived in the Colombo Zoological Gardens for many years, were found by the same workers[21] to be myristic 0·9, palmitic 17·5, stearic 10·1, arachidic 0·6, tetradecenoic 0·9, hexadecenoic 2·1, oleic 62·2, octadecadienoic 5·2 and unsaturated C_{20-22} 0·5 per cent. (wt.). Except for relatively low palmitic and high oleic acid contents, the body fat of the emu is thus similar to those of many of the larger land mammals (*cf.* p. 105). The bird in question had been fed on various grains and concentrates ; the natural diet of the emu is fruit, roots and herbage.

How far the composition of hen fats is an accurate picture of avian body fats in general remains to be seen. The mean equivalents and iodine values, and the melting points of the fats and their mixed fatty acids, recorded in Table 24, suggest that at least there is a strong tendency towards a composition based roughly on the presence of not more than 30 per cent. of saturated (palmitic) acid with 70 per cent. of unsaturated acids (the mean molecular weight of this mixture of fatty acids is about 274). The data as a whole are an eloquent example of the uselessness of average characteristics, and the pressing need for detailed analyses before any real progress can be made in defining and discussing the composition of natural glycerides.

TABLE 24

BIRD DEPOT FAT	FAT		MIXED FATTY ACIDS	
	IODINE VALUE	M. PT.	M. PT.	MEAN MOLECULAR WEIGHT
Hen [19]	77–80	30–32°	34–36°	272–274
Goose, domestic [22a]	66–73	32–34°	35–41°	277
,, wild [23]	67–99		34–40°	285
Turkey [23]	66–81	31–32°	37–38°	275–280
Crane [22b]	71		31°	279
Duck, tame [23]	58–72	27–39°		289
,, wild [23]	84	—	36–40°	282
Starling [23]	84	30–35°	38–39°	268

Effect of ingested dietary fats on the depot fats of birds. It is apparent that birds, like the land mammals, are capable of utilising ingested fat for reserve purposes as well as of synthesising their own characteristic type of fat when reared on a diet which is normally not over-rich in fat. Miss Cruickshank[26] has published data which, although based on observations of mean unsaturation (iodine value) alone, amply prove this in the case of the domestic hen. Before studying the effect of ingested fats of different types, Miss Cruickshank determined the iodine values of the mixed fatty acids from different fat depots in eight individual hens, with the results given in Table 25.

TABLE 25. *IODINE VALUES OF MIXED FATTY ACIDS OF FAT FROM DIFFERENT DEPOTS*

No. of Hen	Gizzard	Neck	Leg Muscle	Abdominal
3	93	92	93	90
15	79	79	—	78
17	64	67	65	65
25	90	90	90	88

No. of Hen	Skin	Neck	Leg Muscle	Abdominal	Gizzard	Kidney	Mesenteric	Epicardial	Av. I.V.	Max. diff. between Depots
5	87·3	88·1	86·2	87·1	84·5	84·4	84·0	85·6	85·9	4·1
8	81·4	78·0	—	—	75·6	77·7	—	—	78·2	5·8
29	92·0	89·9	88·4	88·1	89·0	87·8	88·0	90·2	89·2	4·2
32	85·9	81·7	81·2	80·8	79·7	81·6	80·7	85·7	82·2	6·2

These figures, which are in agreement with the conclusions to be drawn from the detailed component acid data given by Hilditch, Jones, and Rhead [20] for abdominal, gizzard, and neck fats of the hen, indicate that there is comparatively little difference in composition in the fats from any of the depots in the body of the hen. As already pointed out, this uniformity of depot fat composition in different parts of the same bird is in marked contrast to the definite differences in the component acids of depot fats from different adipose tissues of the larger land mammals.

Batches of hens were then fed on diets containing 28 per cent. of either palm kernel oil, mutton tallow, or hempseed oil (the respective iodine values of these fats being 15, 45, and 160). In the case of the two relatively saturated fats, feeding caused a diminution of the iodine value of the depot mixed fatty acids from 81–83 to 51–55 in two months (palm kernel oil diet), and to 59–66 in four to five months (mutton tallow diet). The response to the hempseed diet was more rapid, the iodine value of the depot mixed fatty acids rising to 139–145 within six weeks. Conversely, resumption of the control (low-fat) ration caused a relatively rapid increase to normal iodine values for the depot fatty acids in the course of about a month in the case of hens which had received the palm kernel oil or mutton tallow, whilst about six months elapsed after return to the control diet before the high unsaturation of the depot fatty acids, resulting from the hempseed diet, fell to the normal figure of below 90.

Depot fats of sea-birds. Sea-birds, which of course feed mainly on fish, are probably an instance in which it must be considered that the nature of the depot fat is affected considerably by the circumstance that relatively large amounts of fat are assimilated directly from the diet. Koyama [27] determined the percentage of ether-insoluble bromo-additive products obtained from the "liquid" fatty acids of the depot fats of a number of Japanese land and aquatic birds. The former yielded very small amounts (not exceeding 1 per cent.) of ether-insoluble "polybromides," whereas the sea-bird fats gave much higher yields—up to 10–15 per cent. of products containing about 69 per cent. of bromine.

Lovern[28] has recently carried out detailed analyses of the component acids of some sea-bird depot fats, with the results shown in Table 26.

TABLE 26. *COMPONENT FATTY ACIDS (WTS. PER CENT.) OF SOME SEA-BIRD FATS*

	Fat Content (Per Cent.)	Saturated				Unsaturated				
		C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Gannet (*Sula bassana*)	6·7	3·2	17·1	3·6	—	1·0 (−2·0H)	5·2 (−2·0H)	28·3 (−2·8H)	24·2 (−4·0H)	17·4 (−6·0H)
Fulmar petrel (*Fulmarus glacialis*)	15·2	2·0*	13·9	3·2	—	0·9 (−2·0H)	3·9 (−2·0H)	26·9 (−2·8H)	26·8 (−4·0H)	22·1 (−6·6H)
Skua gull (*Megalestris catarrhactes*)	7·0	1·9	16·4	5·7	0·2	0·4 (−2·0H)	4·6 (−2·1H)	32·6 (−2·6H)	19·7 (−3·3H)	18·5 (−3·8H)
Herring gull (*Larus argentatus*)	9·7	3·3	18·5	6·2	0·2	0·5 (−2·0H)	4·0 (−2·3H)	30·5 (−2·8H)	20·3 (−4·1H)	16·5 (−4·9H)

* 0·3 per cent. of saturated acids (capric) lower than C_{14}.

Lovern has pointed out that all four fats (Table 26) are of the "aquatic" type, and are closely similar in their component acids to the average marine fish fat. The sea-bird fats differ from the latter, however, in unsaturation. The stearic acid content is higher than in fish fats, whilst in two cases arachidic acid (which can hardly have been ingested) appears. Concurrently the degrees of average unsaturation of the C_{20} and C_{22} acids are reduced below the average for fish fats.

The body fat of a penguin has been partly studied by S. Ueno and T. Aoki,[24] who state that the fatty acids included 4 per cent. myristic, 14 per cent. palmitic and 5 per cent. stearic acids, with oleic and "clupanodonic" acids, but hexadecenoic acid was not detected. This partial analysis, and the recorded iodine value (134·2) of the penguin fat, suggest that the fat, like those of the smaller sea-birds examined by Lovern,[28] is similar to that of marine fish on which it feeds.

The sea-birds thus form an exception to the broad rule that fat types can be correlated with phylogenetic relationships. Lovern suggests two possible explanations for this: (*a*) that they have no specific requirements and any type of depot fat will serve equally well, or (*b*) that in the course of evolution their specific requirements have been produced or modified to suit the normal diet.

Bird egg fats. Apart from a few general characteristics which have been reported for the fatty matter present in the eggs of pigeons,[29] ducks and geese,[30] attention has been confined to the egg of the domestic fowl, and even here there is at present little in the way of accurate detailed analysis. Phosphatides (egg yolk lecithin) are of course prominent in egg lipids, but for the most part the recorded analyses do not differentiate between glyceridic and phosphatidic lipids, giving only the mixed fatty acids present in the total fatty matter. The ether-soluble lipids amount to about 30–35 per cent. of the fresh egg yolk (equivalent to about 60–70 per cent. on a moisture-free basis). The amount of phosphatides in the fresh yolk is variously given as from 4 to 12 per cent., the differences being due possibly both to varying technique in the separation of the phosphatides and to genuine differences due to dietary or other variable factors.

The component acids of egg phosphatides (lecithin) have only been studied in one recent instance [37] by the ester-fractionation method, but various estimates based on simpler processes of analysis have been given. (For a more complete summary of the older work, the reader is referred to the monograph of MacLean.[31]) Cousin [32] gives the proportions of egg lecithin fatty acids as palmitic 29, stearic 14, oleic 33, and linoleic 24 per cent. Levene and Rolf,[33] and also Hatakeyama,[34] state that linoleic acid is present only in subordinate amounts, and that arachidonic acid is a component acid (but, according to Levene and Rolf, not in so large proportions as in animal liver phosphatides, *cf.* p. 108). Sueyoshi and Furukubo [35] calculated (from the bromo-additive products obtained from the unsaturated acids) that egg lecithin (freed from kephalin as well as glycerides) contained the following unsaturated acids: oleic 73, linoleic 2, and "clupanodonic" 5 per cent.; this of course implies that the actual contents of the two latter acids would have been somewhat greater, say, respectively, about 4 and 7 per cent. All that can be deduced from these observations is that the egg phosphatide fatty acids seem to be similar qualitatively to those of animal livers (*cf.* p. 108) and that, apart from possibly low proportions of unsaturated C_{20} and C_{22} acids, they may have considerable quantitative resemblance to the latter. An examination by the modern methods would doubtless also reveal the presence of some hexadecenoic acid, in addition to providing a more accurate picture of the other main component acids.

The fatty acids of egg glycerides were examined by Grossfeld,[36] who determined the percentage of saturated acids and the iodine and thiocyanogen values of the unsaturated acids, and calculated his results* to a mixture of the following acids: palmitic 32·0, stearic 2·2, oleic 43·6, *iso*-oleic 1·4, linoleic 17·7, and linolenic 3·1 per cent. Taking into account the fact that no allowance has been made for myristic, hexadecenoic or unsaturated C_{20} and C_{22} acids, these figures are not very different from those for the hen depot fat component acids in Table 23 (p. 71).

Miss Cruickshank,[26] employing a similar method of analysis to Grossfeld, obtained the following figures for the total mixed fatty acids of egg yolks from hens fed on control rations containing respectively 3·8 per cent. and 2·3 per cent. of fatty matter: †

	PER CENT. (WT.)	PER CENT. (WT.)
Saturated acids *	31·4	31·2
Oleic acid	46·7	51·4
Linoleic acid	19·0	15·0
Linolenic „	2·9	2·4
(* Mean molecular weight of saturated acids.	263·5	264·0)

In 1938 an analysis of the fatty acids of both glycerides and phosphatides of egg yolk was carried out by the modern methods by Riemenschneider, Ellis, and Titus,[37] with the following results:

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* Unsaturated acids calculated according to Kaufmann's assumed thiocyanogen values for linoleic and linolenic acids.

† Another analysis of "egg oil fatty acids," by Trost and Doro (*Annali. Chim. Appl.*, 1937, **27**, 233) gives the component acids as: myristic 2, palmitic 29, stearic 9, arachidic 0·1, hexadecenoic 12, oleic 35, linoleic 10 per cent. (wt.).

	Component Acids, Wt. (Per Cent.)		Component Acids, Mol. (Per Cent.)	
	Glycerides	Phosphatides	Glycerides	Phosphatides
Myristic	0·7	—	0·8	—
Palmitic	25·2	31·8	27·0	34·6
Stearic	7·5	4·1	7·3	4·0
Hexadecenoic	3·3	—	3·6	—
Oleic	52·4	42·6	51·0	42·0
Linoleic	8·6	8·2	8·4	8·2
Clupanodonic	2·3	13·3	1·9	11·2

The evidence indicated the presence of " clupanodonic " acid rather than of " arachidonic " acid, and it will be seen that, as usual, there is more of this acid in the phosphatides than the glycerides. At the same time the total proportion of saturated acids is somewhat greater in the phosphatides (38·6 per cent. mol.) than in the glycerides (35·1 per cent. mol.). The component acids of the egg yolk glycerides are on the whole similar to those of the hen depot fat glycerides in Table 23, but the oleic acid content is greater (mainly at the expense of linoleic and hexadecenoic acids).

Effect of ingested dietary fat of hen on egg lipids. The effect of added fat in the diet of the hens has been observed materially to alter the composition of the egg lipids. Henriques and Hansen [38] found that the iodine value of the egg phosphatides was unchanged when linseed or hempseed was fed to the hen, but the iodine values of the egg glycerides increased as follows :

Feeding	Iodine Value of Egg Glycerides
Carbohydrate diet	79
Linseed	97
Hempseed	119–123

McCollum, Halpin, and Drescher,[39] and also Terroine and Belin,[40] however, found that the iodine values of both the glycerides and the phosphatides in the egg were lower when the hens were on a fat-free diet than when they were receiving a normal ration containing about 3–4 per cent. of fatty matter.

Miss Cruickshank,[26] again using the determination of saturated acids combined with the iodine and thiocyanogen values of the unsaturated fatty acids, examined the mixed fatty acids from the total lipids of eggs from hens fed on the following different rations :

Control ration	(bran, maize, sharps, and Sussex ground oats, with 7 per cent. extracted soya bean meal, 7 per cent. fish meal, and 3 per cent. mineral mixture).
Fish meal-free ration	(degermed maize, bran, whole yeast, rice, alfalfa, with 7 per cent. extracted soya bean meal and 3 per cent. mineral mixture).

Control ration+28 per cent. palm kernel oil.
,, ,, +28 per cent. palm oil.
,, ,, +28 per cent. mutton fat.
,, ,, +28 per cent. linseed oil.
,, ,, +28 per cent. hempseed oil.
Hempseed alone.

The component acids of the dietary fats were approximately as follows :

Component Acids, (Wt. Per Cent.)	Palm Kernel Oil	Palm Oil	Mutton Fat	Linseed Oil	Hempseed Oil
Saturated	81	46·3	51·0	9·2	6·1
Oleic	18	46·4	46·8	26·6	12·0
Linoleic	Trace	7·3	2·2	13·4	68·5
Linolenic	—	—	—	50·8	13·4

* Unsaturated acids calculated according to the empirically determined thiocyanogen values for linoleic and linolenic acids (" T," Chapter IV, p. 138).

The data recorded for the egg yolk mixed fatty acids are given in Table 27.

TABLE 27. *COMPOSITION OF MIXED FATTY ACIDS OF EGG YOLK**

		Control Mash	Fish Meal-free Mash	Mash+ Palm Kernel Oil	Mash+ Palm Oil	Mash+ Mutton Fat	Mash+ Linseed Oil	Mash+ Hemp Oil	Hempseed Alone
Mixed acids	I.V.	84·4	80·0	80·5	85·9	84·0	123·1	115·7	127·2
	Mol. wt.	280·5	283·0	280·3	281·4	284·0	281·8	282·1	280·6
"Solid" acids	Per cent.	31·4	31·2	30·3	27·8	29·5	23·9	24·3	21·4
	Mol. wt.	263·5	264·0	266·4	265·5	268·0	265·7	267·4	266·0
"Liquid" acids	I.V.	121·2	115·9	115·0	120·0	117·7	161·3	156·3	162·8
	Mol. wt.	278·2	284·0	278·8	280·0	283·3	283·4	281·1	278·9
	CNS value	94·0	93·3	92·3	90·8	93·7	111·2	96·4	101·8

PERCENTAGE COMPOSITION (WT.) OF MIXED FATTY ACIDS

	Control Mash	Fish Meal-free Mash	Mash+ Palm Kernel Oil	Mash+ Palm Oil	Mash+ Mutton Fat	Mash+ Linseed Oil	Mash+ Hemp Oil	Hempseed Alone
Saturated acids	31·4	31·2	30·3	27·8	29·5	23·9	24·3	21·4
Oleic acid	47·4	51·1	51·4	48·6	51·4	37·9	23·5	25·3
Linoleic acid	19·0	15·9	17·6	23·6	17·0	17·4	49·6	44·1
Linolenic acid	2·2	1·8	0·7	—	2·1	20·8	2·6	9·2

These figures, in spite of some lack of detail and the necessarily arbitrary method of evaluation, are of great comparative interest, especially in conjunction with the corresponding data for hen depot fat (pp. 70, 71). In the first place, although the data refer to eggs from hens which had been receiving the various diets for at least six weeks, it was established by independent tests that the alteration in the egg lipids, due to added dietary fat, is complete in sixteen days. As regards the various fats fed to the fowls, it is evident that, in contrast to the hen depot fats, only the constituents of the more unsaturated dietary fats passed readily into the ova fatty acids; ingestion of linseed and hempseed oil led to considerable increases in the linoleic and linolenic acid contents of the egg lipids. The more saturated fats had comparatively little influence on the composition of the egg fatty acids, apart from a slight *diminution* in the percentage of saturated acids and an increase in linoleic acid content when palm oil (with 7 per cent. of that acid) was present in the diet. It is particularly notable that the presence of 40 per cent. of palmitic acid in the palm oil, or of 51 per cent. of palmitic and stearic acid in the mutton fat, caused no increase, but rather a slight fall in the saturated acids of the egg lipids, the oleic acid content of which remained almost unchanged; whilst the proportions and the average molecular weight of the saturated fatty acids of the egg yolks from hens receiving palm kernel oil show that myristic, lauric, and lower saturated acids (which amount to 70 per cent. of the total fatty acids of this oil) were not transmitted in appreciable amounts to the ova.

Although the absence of any data for hexadecenoic acid makes definite conclusions somewhat difficult, it may be gathered from the amount (ca. 30 per cent. wt.) and mean molecular weight (263–265) of the saturated acids in these egg fat analyses that the proportion of palmitic acid in the total fatty acids is of the order of 25 per cent. (wt.), and that therefore its molar percentage is about 27 per cent.—a figure similar to that for hen depot fats and not far below that of 30 per cent. (mol.), which is characteristic for the depot fats of the land mammals.

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* Unsaturated acids calculated according to the empirically determined thiocyanogen values for linoleic acids ("T," Chapter IV, p. 138).

The evidence given by the above analyses suggests that more complete analyses by the modern methods of the egg lipids of more than a single species of bird, after resolution as far as possible into glyceridic and phosphatidic fractions, cannot fail to yield interesting and fruitful results.

DEPOT FATS OF RODENTS

The detailed study of component acids of rodent depot fats is almost confined to those of one species—the white rat which is employed so largely in the biological evaluation of vitamins A and D. This circumstance accounts for the comparatively large amount of work which has been carried out on the fats of this animal, and it is unfortunate that, as usual, the abundant data for this species are counterbalanced by an almost complete absence of reliable figures for the fats of any other member of this group. This is the more to be regretted since, if we may take the white rat as typical, it is clear that rodents share with birds a kind of depot fat which, in its reduced but still appreciable content of hexadecenoic acid, is definitely intermediate in type between the reserve fats of amphibia and reptiles and those of the higher land mammals ; whilst its content of palmitic acid already approximates to the 30 per cent. characteristic of fats of the latter category of animals. However, the data available for rat depot fats render possible an interesting outline of, in the first place, the typical component acids of such fats from animals on diets low in fat and, secondly, of the effect of added dietary fat upon the composition of the depot fat.

Rat depot fats (from animals on low fat diets). The data here come from five sources :

(i) Banks, Hilditch, and Jones [41] (1933). These were combined adipose tissue fats dissected from the subcutaneous, perinephric and mesenteric areas of rats grown on various diets for biological testing purposes in the laboratory of Professor J. C. Drummond. The diets represented were as follows :

Group A. Fat-free diet, apart from daily doses in some cases of 15 mgm. of ethyl laurate.

Group B. Various diets very low in fat, but in a few cases 10 per cent. of the diet was hydrogenated cottonseed oil.

Group C. Fed for 12 weeks on a special diet including as the only fatty component 2 per cent. of cod liver oil (an amount which produced no perceptible alteration in the depot fat composition).

(ii) Klenk, Ditt, and Diebold [12b] (1935). Rat body fat from animals on a low fat ration.

(iii) Spadola and Ellis [42] (1936). Rat adipose tissue fat from animals on a ration of casein 18 per cent., dextrin 64 per cent., agar 1 per cent., salt mixture 4 per cent., alfalfa leaf meal 5 per cent., yeast 8 per cent.

(iv) Longenecker and Hilditch [43] (1938). Total carcass fat of rats fed wholly on a cow milk diet. (This fat again showed little divergence from normal as a result of the ingested cow milk fat and is therefore included in this group.)

In the analyses of Banks *et al.*, the " solid " and " liquid " esters were distilled from a Willstätter bulb and algebraic calculations made to determine the proportions of hexadecenoic and other acids present. Klenk *et al.*, and Spadola and Ellis, employed the electrically heated column described (*cf.* Chapter XI, p. 478) by Jantzen and Tiedcke, whilst Longenecker and Hilditch used an electrically heated and specially packed column (*cf.* Chapter XI, p. 479) which permits the detection of traces of component acids which may otherwise escape notice. (In Table 28A, which gives a summary of the results obtained by groups (i)–(iv) of the above workers, the latter results are included in their fully detailed form.)

(v) Longenecker [44] (1939). Here an elaborate scheme of feeding and fasting trials was undertaken, followed by detailed component acid determinations on the rat body fats, on groups of male and female albino rats:

Male group. 1. Rats fed from weaning to a body weight of about 275 gm. on a balanced diet containing 5 per cent. of fat (in which linoleic glycerides were present);

2. Group 1, fasted until 28 per cent. loss in body weight.
3. Group 1, fasted until 17 per cent. loss in body weight.
4. Group 1, fasted until 24 per cent. loss in body weight, then fed on a diet very rich in carbohydrate (sucrose).
5. Group 1, fasted until 27 per cent. loss in body weight, then fed on a diet very rich (96 per cent.) in protein (casein).
6. Rats raised on the stock diet to 240 gm. body weight, then fed on the high sucrose diet for the same time (27 days) as the group 4 animals.

Female group. 1. Rats fed from weaning to a body weight of about 190 gm. on same stock diet as male group 1.

2. Group 1, fasted to 30 per cent. loss of body weight, then again fed the stock ration.
3. Rats, at weaning, fasted for a short time and then fed on a very low fat, high carbohydrate (maize starch) diet.
4. Group 3, fasted to 22 per cent. loss of body weight.

The body fat component acids (molar percentages) of these 10 groups of rats are given in Table 28B.

TABLE 28A. *COMPONENT ACIDS (WTS. PER CENT.) OF DEPOT FATS OF RATS ON LOW FAT DIETS*

	BANKS, HILDITCH, AND JONES [41] GROUP A	BANKS, HILDITCH, AND JONES [41] GROUP B	BANKS, HILDITCH, AND JONES [41] GROUP C	KLENK *et al.* [3]	SPADOLA AND ELLIS [42]	LONGENECKER AND HILDITCH [43]
Decanoic	—	—	—	—	—	0·3
Lauric	—	—	—	—	—	0·7
Myristic	5	4·5	4	2	5·6	6·9
Palmitic	24	28	30	25	29·3	24·3
Stearic	3	2	2·5	3·5	2·5	5·3
Arachidic	—	—	—	—	—	1·2
Tetradecenoic	—	—	—	—	—	1·2
Hexadecenoic	8	7	8·5	13	14·0	5·6
Oleic	58	58·5	53	55	48·6	49·1
Octadecadienoic	2	—	2		—	4·9
C_{20-22} unsaturated	—	—	—	1·5	—	0·5

TABLE 28B. *COMPONENT ACIDS (MOLS. PER CENT.) OF DEPOT FATS OF RATS ON LOW FAT DIETS*

(Longenecker,[44] 1939.)

MALE GROUP

Diet, etc.	1 Stock diet.	2 1, fasted to 28 per cent. loss.	3 1, fasted to 17 per cent. loss.	4 1, fasted to 24 per cent. loss, then sucrose diet.	5 1, fasted to 27 per cent. loss, then casein diet.	6 Stock diet, then high sucrose diet.
Myristic	1·6	1·8	2·0	3·1	2·8	2·7
Palmitic	21·6	21·8	21·6	26·7	29·7	28·2
Stearic	3·6	3·7	4·6	3·6	3·8	4·3
Arachidic	2·0	1·2	1·6	0·4	1·1	1·2
Tetradecenoic	—	0·3	0·8	0·9	1·0	1·2
Hexadecenoic	4·1	4·8	5·7	15·6	15·6	12·2
Oleic	51·9	51·3	43·4	47·2	43·8	42·0
Octadecadienoic	13·0	13·5	19·2	2·2	2·0	8·0
C_{20-22} unsaturated	2·2	1·6	1·1	0·3	0·2	0·2

Female Group

Diet, etc.	1 Stock diet.	2 1, fasted to 30 per cent. loss.	3 High carbohydrate (maize starch).	4 3, fasted to 22 per cent. loss.
Myristic	1·8	3·1	2·9	4·0
Palmitic	24·4	23·0	30·4	28·8
Stearic	3·6	7·2	4·9	4·6
Arachidic	0·8	0·7	—	0·3
Tetradecenoic	0·3	1·7	1·3	1·9
Hexadecenoic	4·8	10·0	13·1	7·2
Oleic	44·3	39·9	46·0	51·0
Octadecadienoic	18·6	13·3	1·4	2·2
C_{20-22} unsaturated	1·4	1·1	—	—

The component acids of body fats of rats fed on low fat diets exhibit several points of interest.

(i) As in the hen depot fats, the palmitic acid content is approximately 30 per cent. (molar)—the figure which, as we shall see, is characteristic for nearly all land animal depot fats so far studied.

(ii) The type of " synthetic " fat laid down by the rat from a carbohydrate or protein (probably *via* carbohydrate) diet is well illustrated by the data of Spadola and Ellis (Table 28A) and of Longenecker (Table 28B, male groups 4 and 5, female group 3). This is remarkable not only for the close approximation to 30 per cent. (mol.) of palmitic acid, but still more for the high proportion of hexadecenoic acid (13–15 per cent.). Moreover, this high figure for hexadecenoic acid is only attained when the diet contains 1 per cent. or less of fat—in other low fat diets in which the fat content may have approached 5 per cent. of the whole diet, the hexadecenoic acid content of the body fat was reduced to about 5–8 per cent.

(iii) The utilisation of fat reserves during fasting (*cf.* Table 28B) seems on the whole to involve most of the component acids more or less indiscriminately, although some slight but indefinite evidence of selective mobilisation appears here and there. Other evidence on the mobilisation of constituents of depot fats during inanition will be found below in the case of rat fats, and later in this chapter (p. 99) in the case of pig fats.

(iv) The proportions of polyethenoid C_{18} and C_{20} acids in the rat body fats are also of much interest. Those of the C_{20} and C_{22} series vary from almost *nil* to about 2 per cent., whilst the most striking feature, possibly peculiar to the rat, is its inability to synthesise linoleic or other diethenoid C_{18} acids. When linoleic glycerides are present in the dietary fat, however, they appear to pass readily into the fat depots of the rat ; probably the moderate proportion of octadecadienoic acid in the body fat of rats fed on cows' milk (Table 28A), and the comparatively high proportion of this acid in the body fats of the rats (Table 28B) fed on Longenecker's stock diet, arise from direct assimilation. Similarly, in the fats of some wild rodents (*v. infra*) linoleic or other polyethenoid C_{18} acids are present in quantity. Fat synthesised by the rat from carbohydrate, however, appears to be deficient in octadecadienoic acid, which only then occurs to the extent of 1–2 per cent. of the total fatty acids.

It was established by Burr and Burr [45] that a supply of linoleic or similar diethenoid acid is essential to the health of the rat, and this observation has led to many other biochemical studies as to the function of linoleic acid in the lipids of the animal. The idiosyncrasy of the rat as regards ability to synthesise and store linoleic acid is, however, not by any means clearly understood. Gregory and Drummond,[46] for example, showed that on a fat-free diet the animal produces linoleic or other diethenoid C_{18} acid in its liver lipids, but does not store them in its adipose tissues. Yet Spadola and Ellis [42] (*cf.* Table 29A) found that the linoleic acid of ingested cottonseed oil was readily deposited in the adipose tissue, an observation which is also confirmed by the data of Banks *et al.*[41] and of Channon, Jenkins, and Smith.[47]

Subsequently, Nunn and Smedley-MacLean [50] found that rats on a fat-free diet yielded liver fats with no tetra- or penta-ethenoid acids, but that on the same diet with the addition of a little methyl linoleate, the liver fats contained some arachidonic acid ($C_{20}H_{32}O_2$), whilst with the addition of methyl linolenate, both arachidonic and docosapentaenoic ($C_{22}H_{34}O_2$) acids appeared in the liver fats. They say: "Linoleic and linolenic acids appear to be the building stones essential for the production of more highly unsaturated acids (with chains of more than 18 carbon atoms) which play some unknown part in enabling the animal to store fat in its depots and tissues." This is strikingly supported by Longenecker's results (Table 28B), in which the arachidonic acid contents of the body fats were almost negligible (nil–0·3 per cent.) when almost exclusively carbohydrate or protein diets had been given, whereas the stock diet which led to the appearance of a fairly high proportion of octadecadienoic acid also led to the presence of appreciable amounts (1·4–2·2 per cent.) of arachidonic acid. Later, Smedley-MacLean *et al.*[50] have put forward evidence which suggests that the highly unsaturated C_{20} or C_{22} acids are more efficient promoters of growth in the rat than linoleic acid but, although necessary for the formation of new tissue, may not be essential to maintain the normal metabolism of the cell.

Rat depot fats (from animals on diets which included various fats). The following data may be considered here:

(i) Banks, Hilditch, and Jones [41] (1933). Adipose tissue fats (as above, p. 78) from a group (C) of rats which had received diets containing from 2 to 15 per cent. (usually 5 per cent.) of cod liver oil for 10 weeks.

(ii) Spadola and Ellis [42] (1936). Adipose tissue fats from rats fed for 10 weeks on the basal diet (above, p. 78) in which 8 per cent. of dextrin was replaced by 8 per cent. of cottonseed oil, non-hydrogenated or hydrogenated to two different stages.

The component acids of the cottonseed oils employed were as follows (wts. per cent.):

	SATURATED	OLEIC (WITH *Iso*-OLEIC)	LINOLEIC
Non-hydrogenated (B)	28·8	22·7	48·5
Hydrogenated (C)	35·5	52·5	12·0
„ (D)	35·4	62·3	2·3

(iii) Channon, Jenkins, and Smith [47] (1937). Total carcass fats of rats whose diet included 40 per cent. of either beef depot fat, palm oil, olive oil, cod liver oil, butter fat or coconut oil, for 14 days.

(iv) Longenecker and Hilditch [43] (1938). Total carcass fats of rats fed wholly on cow milk diet (data already given in Table 28A).

(v) Longenecker [44] (1939). Rats reared on a balanced stock diet and then fasted until they had lost nearly 30 per cent. of their body weight were fed on diets very high in, respectively, maize oil and coconut oil (the fats were calculated to provide 84 per cent. of the calories, the remaining 16 per cent. of calories in the diet coming from casein). Some of the animals were killed and the body fats analysed, whilst others were fasted to varying degrees before their depleted body fats were examined (Table 29B).

TABLE 29A. *COMPONENT ACIDS (WTS. PER CENT.) OF DEPOT FATS OF RATS ON SPECIFIC FATTY DIETS*

OBSERVERS :	BANKS *et al.* [41]	SPADOLA AND ELLIS [42]		
INGESTED FAT	COD LIVER OIL	COTTONSEED OIL	HYDROGENATED COTTONSEED OIL	
		B	C	D
Per cent. fat in diet	2–15	8	8	8
Component acids—				
Myristic	5	3·4	4·6	4·3
Palmitic	23	32·8	25·8	26·4
Stearic	2·5	3·4	1·6	2·0
Arachidic	—	—	0·2	0·2
Hexadecenoic	5·5	2·0	6·8	8·8
Oleic	51·5	30·2	52·3	54·4
Octadecadienoic	4	27·3	8·3	3·3
C_{20-22} unsaturated	8·5	0·9	0·4	0·6

	OBSERVERS : CHANNON, JENKINS, AND SMITH [47]					
INGESTED FAT	BEEF FAT	PALM OIL	OLIVE OIL	COD LIVER OIL	BUTTER	COCONUT OIL
Per cent. fat in diet	40	40	40	40	40	40
Component acids—						
Lauric	—	0·1	—	—	0·1	7·8*
Myristic	1·1	2·1	0·1	1·6	3·5	13·4
Palmitic	22·7	20·8	17·1	15·6	25·9	18·1
Stearic	6·2	6·9	4·0	5·4	4·2	5·0
Arachidic	1·6	1·0	0·7	2·5	1·5	1·3
Behenic	—	0·7	0·5	—	—	—
Hexadecenoic	2·5	4·7	4·2	9·5	5·0	3·1
Oleic	52·5	37·1	49·4	38·4	40·1	31·5
Octadecadienoic	2·6	8·8	7·3	10·6	6·0	10·4
C_{20} unsaturated	10·5	14·0	13·8	11·8	10·3	6·9
C_{22} ,,	—	—	—	2·7	—	—

* Also 0·9 per cent. decanoic acid.

TABLE 29B. *COMPONENT ACIDS (MOLS. PER CENT.) OF DEPOT FATS OF RATS ON SPECIFIC FATTY DIETS.*

(Longenecker,[44] 1939).

INGESTED FAT	MAIZE OIL			COCONUT OIL		
	1	2	3	1	2	3
	High fat diet.	1, fasted to 14 per cent. loss.	1, fasted to 24 per cent. loss.	High fat diet.	1, fasted to 15 per cent. loss.	1, fasted to 30 per cent. loss.
Decanoic	—	—	—	0·7	0·7	1·0
Lauric	—	—	—	31·8	24·5	23·0
Myristic	0·7	0·7	0·7	18·1	19·6	15·4
Palmitic	12·2	14·1	11·8	18·6	19·4	15·8
Stearic	2·9	1·5	2·0	2·7	1·7	5·2
Arachidic	0·2	1·4	1·5	0·6	0·5	0·9
Dodecenoic	—	—	—	0·6	0·4	0·5
Tetradecenoic	—	0·4	—	1·5	0·9	1·1
Hexadecenoic	6·9	4·2	5·4	4·1	3·8	4·3
Oleic	44·8	46·5	48·8	20·1	26·9	30·7
Octadecadienoic	32·3	31·2	29·8	1·2	1·6	2·1

It seems possible to draw certain general conclusions from the rather complicated data quoted in Tables 29A and 29B.

(i) Polyethenoid C_{18} acids were readily assimilated from those diets in which they were present (notably cod liver, maize, cottonseed, palm and olive oils). In the fat-depleted (fasted) rats fed by Longenecker on maize oil, the composition of the body fat differed but little from that of the ingested oil. Again, the amount of linoleic glycerides deposited, in relation to the proportion in the ingested fats, was especially high in the case of Spadola and Ellis's cottonseed oil experiments and in the palm and olive oil diets given by Channon *et al.* (The high linoleic figure for the rat fat in the latter group from a coconut oil diet appears remarkable, since coconut oil itself contains only about 1 per cent. of linoleic acid; this anomaly does not appear, however, in Longenecker's data.)

(ii) The highly unsaturated C_{20} and C_{22} acids of cod liver oil are evidently also assimilated and deposited to a marked extent. (It will be noted that Channon and co-workers observed much higher contents of C_{20} unsaturated acids in all their rat fats than have been recorded by other workers; this feature does not seem to be adequately explained by the authors' note that the total body fats (including phosphatides) were analysed, since this also applies in most of the other analyses in Tables 28 and 29.)

(iii) Lauric acid was not stored to any marked extent when coconut oil formed 40 per cent. of the diet (Channon *et al.*), but lauric glycerides formed about 30 per cent. of the depot fat when coconut oil formed almost the entire diet (Longenecker). Lauric acid is thus definitely less utilised in depot fats than the higher fatty acids, whilst the C_{10} and lower saturated acids of coconut oil or cow milk fat are to all intents and purposes not stored by animals in their reserve fats.

An interesting point noted by Longenecker [44] is the appearance of traces of dodecenoic acid and of about 1 per cent. of tetradecenoic acid in the rat body fats from coconut oil feeding—pointing to the occurrence, to a small extent, of desaturation of the corresponding saturated glycerides ingested by the animals.

(iv) In view of the ready influx of ingested unsaturated acids to the depots, it is natural that, when feeding the more unsaturated oils (e.g. olive or cod liver oils), the percentage of palmitic acid is often substantially reduced. It seems significant, however, that a diet including 40 per cent. of beef fat or palm oil (in which palmitic respectively forms about 30 per cent. and over 40 per cent. of the component acids) has also resulted in *diminishing* the palmitic acid content to below the normal figure. This is not peculiar to rat fats, and it will be seen later (p. 100) that an exactly parallel result has been obtained by feeding cottonseed oil to pigs, the resulting depot fat containing a lower proportion of palmitic acid than either normal pig depot fat or the ingested cottonseed oil. (This effect is not, however, discernible in Spadola and Ellis's cottonseed oil experiments on rats.) This suggests several important considerations, namely, that the "normal" content of about 30 per cent. of palmitic acid in animal depot fats is conditioned mainly by the fat actually synthesised by an animal; that this figure is attained only when the diet is "balanced" in so far that it does not contain more than a certain proportion of preformed fat; and that feeding of rations with a high fat content (irrespective of the capacity of the animal to store considerable proportions of the ingested fat) causes interference with the normal production of fat in the animal, and must therefore be regarded as definitely abnormal, if not almost pathological.

(v) Further interesting evidence on the utilisation of the different constituents of reserve fats by the rat during fasting will be found in Table 29B.

In the rats fed on maize oil, the body fats of which contained mainly oleic and linoleic acids, no marked changes in the relative proportions of these acids occurred during inanition, and little selectivity appeared to be made from the available component fatty glycerides. In this respect the behaviour of this group of rats resembled that of those on low fat diets (Table 28B).

With rats whose body fat was largely derived from coconut oil, Longenecker observed a marked difference. Here the percentage of lauric, myristic, palmitic and oleic acids withdrawn during fasting from the amounts of these acids present in the body fats of the rats before fasting commenced was as follows :

FASTING TO	15 PER CENT.	30 PER CENT.
	(LOSS IN BODY	WEIGHT)
	PER CENT. LOST	PER CENT. LOST
Lauric	53·1	74·4
Myristic	33·3	69·9
Palmitic	35·8	70·1
Oleic	19·1	46·2

These results appear to give unqualified support to the view that saturated acids of lower molecular weight are preferentially utilised ; but Longenecker points out that the circumstance that mixed glycerides are being removed may complicate the issue. Since lauric, myristic and palmitic acid together form 70 per cent. of the total fatty acids (lauric acid itself forming 32 per cent.), it is possible that in this case unselective removal of one molecule at a time of the depot fat mixed glycerides would lead to much the same result.

Nevertheless, it seems more probable that the data for this group of rat body fats imply more ready removal of the glycerides rich in C_{12} and C_{14} saturated acids, just as these (and still more the lower members of the saturated series) are deposited with less ease in the animal fat reserves.

Other Rodent Depot Fats

Wild rabbit (perinephric) fat. A specimen of this fat was studied in detail in 1928 by Vickery,[48a] who found that it was very unsaturated, almost liquid at the ordinary temperature, with a saponification equivalent of 285·2 and an iodine value of 124. The component acids included myristic (4·5 per cent.), palmitic (23 per cent.), and stearic (4 per cent.), with 68·5 per cent. of unsaturated acids which had a mean iodine value of 189·3. The latter were not completely identified, but linoleic acid was present in quantity (probably 35–50 per cent. of the mixed acids), and linolenic acid was also probably present to the extent of nearly 20 per cent. of the total fatty acids, since ether-insoluble hexabromides were isolated equivalent to 9 per cent. of linolenic acid in the total fatty acids. The possible occurrence of any hexadecenoic acid in this fat was, unfortunately, not investigated in this instance.

This rabbit perinephric fat closely resembles the above rat fats in its general content of about 30 per cent. saturated and 70 per cent. unsaturated acids, and in its low stearic acid content. It is quite dissimilar from rat fat in the highly unsaturated character of its C_{18} unsaturated acids ; how far the unsaturation of the C_{18} acids in the depot fats of animals of the same species is dependent upon their state of life (wild or domesticated, etc.) is a matter which is not yet too clear (*cf.* Chapter VIII, p. 355).

The body fat of healthy guinea pigs (*Cavia cutleri*, Caviidæ) was found by Baldwin and Longenecker[48b] to contain as component acids: lauric 1·1, myristic 5·3, palmitic 19·4, stearic 5·7, tetradecenoic 0·8, hexadecenoic 2·1, oleic 36·2, octadecadienoic 18·8, octadecatrienoic 1·2, and unsaturated C_{20-22} acids 9·4 per cent. (wt.). That of guinea pigs suffering from scurvy did not differ materially in composition.

The only other rodent fats for which any characteristics seem to have been given, namely, the hare and the marmot, seem to lend support to the view that wild animals develop relatively unsaturated depot fats:

	Fat		Mixed Acids	
	Sap. Equiv.	Iod. Val.	M.M.W.	Iod. Val.
Hare[49a]	ca. 280	102–119	269	90–98
Marmot[49b]	282–286	93–111	268–277	105

So far as these average data permit one to judge, it seems that the proportions and nature of the saturated acids present in both fats may resemble those in the above rabbit and rat fats.

Depot Fats of the Larger Land Animals

The patchiness of the existing data on the depot fats of land animals will be appreciated when it is pointed out that there are only two or three detailed analyses extant for the depot fatty acids of any carnivorous animal, whilst in the herbivorous group there are a few detailed records for fats from the horse, camel, reindeer, etc., together with a relatively large number of full component acid analyses of the depot fats of oxen, sheep, and pigs. It is much to be desired that adequate data for a wide range of depot fats of the carnivora, and for a wider range of the corresponding fats of the herbivora, should be collected—an aim which should not be very difficult to attain in co-operation with zoological authorities.

Nearly all the detailed records of animal depot fats (including those of oxen, sheep, and pigs) refer only to palmitic, stearic, oleic, linoleic, and myristic acids as the component acids; but it has recently been found that small proportions of hexadecenoic and of unsaturated C_{20} acids are also present. The detailed analyses must accordingly be regarded as belonging to two categories: (*a*) the full statements (at present restricted to a few depot fats) which take account of all the minor components at present detected, and (*b*) the majority of the analyses, which refer chiefly to the major components and which must, in the light of the recent work, be considered as a first approximation to the more complete statement of the whole of the component acids. The latter group are quite serviceable in that they indicate, within reasonably narrow limits, the quantitative proportions of the major component acids.

Depot Fats of the Herbivora

The recorded figures for the fatty acid compositions in this group may be considered conveniently as follows: (*a*) the data for fats from a number of animals, other than those of oxen, sheep, and pigs; (*b*) the more numerous analyses of the body fats of oxen, sheep, and pigs (followed, in the case of the last-named, by consideration of the influence of various fatty diets upon the composition of pig depot fats).

Data have been recorded for fats from various parts of the animals listed in Tables 30A (older analyses, including also one of the hoof fat of the ox) and 30B (fully detailed analyses).

TABLE 30A. *COMPONENT ACIDS (WTS. PER CENT.) OF VARIOUS FATS FROM HERBIVOROUS ANIMALS*

(OLDER ANALYSES)

(EXCLUDING OX, SHEEP, AND PIG DEPOT FATS)

	SATURATED				UNSATURATED		
	C_{14}	C_{16}	C_{18}	C_{20}	OLEIC	LINOLEIC	LINOLENIC
Equidæ—							
Horse (*Equus caballus*)							
Body[51]	—	29	7	—	55	7	2
Abdominal (Western Range, U.S.A.[52])	—	28	5	—	50	13	4
Camelidæ—							
Camel (*Camelus dromedarius*)							
Hump[53]	—	37	16	—	47	—	—
Cervidæ—							
Reindeer (*Cervus tarandus*							
Loin[54]	7	35	20	1	37	—	—
Bovidæ—							
Ox (*Bos taurus*)							
Hoof (Neat's foot oil)[55]	—	18	3	—	79	—	—
Goat (*Capra domestica*)							
Back fat[56]	2·1*	25·5	28·1	2·4	38·4	—	—

* Also 3·5 per cent. lauric acid.

TABLE 30B. *COMPONENT ACIDS (WTS. PER CENT.) OF VARIOUS FATS FROM HERBIVOROUS ANIMALS*

(DETAILED ANALYSES)

(EXCLUDING OX, SHEEP, AND PIG DEPOT FATS)

	SATURATED			UNSATURATED			
	C_{14}	C_{16}	C_{18}	C_{16}	OLEIC	OCTADECADIENOIC	C_{20-22}
Macropodidæ—							
Kangaroo (*Macropus major*)							
Body[21]	4·7 *	25·5	14·1	2·7	45·5	2·6	2·8
Procyonidæ—							
Giant panda (*Ailuropoda melanoleuca*)							
Abdominal[21]	5·0 †	26·4	6·7	3·6	45·1	11·9	—
Ursidæ—							
Ceylon sloth bear (*Melursus ursinus*)							
Body[21]	2·6	28·7	3·4	10·6 ‡	50·5	1·0	1·8

* Also 0·2 per cent. lauric, 1·5 per cent arachidic, and 0·4 per cent. tetradecenoic acids.
† Also 0·4 per cent. lauric and 0·9 per cent. tetradecenoic acids.
‡ Also 1·4 per cent. tetradecenoic acid.

Though the precision of some of the earlier analyses in Table 30A may be regarded as somewhat uncertain, the figures for the horse, camel, and reindeer depot fats conform roughly with the generalisation (which appears more clearly in the depot fats of oxen, sheep, and pigs, Tables 31–35) that palmitic acid forms about 30 per cent. of the total fatty acids in the depot fats of herbivorous animals. The rest of the acids belong almost wholly to the

C_{18} series, the proportion of stearic acid being somewhat variable. The amount of polyethenoid C_{18} acids is also apparently variable, but usually small in comparison with the proportion of oleic acid.

The oil from the hooves of oxen (neat's foot oil) is clearly quite different in composition from the depot fats (*v. infra*) and contains a much larger proportion of oleic acid.

The characteristics of fats from various tissues of another species of deer, the Virginia white-tailed deer (*Odocoileus virginianus borealis*) have been recorded by Treadwell and Eckstein,[57] from which the proportions of saturated, oleic and linoleic acids appear to be approximately as given below:

	Iodine Value	Thiocyanogen Value	Component Acids		
			Saturated	Oleic	Linoleic
Pericardial fat	193·9	29·1	70	27	3
Perirenal ,,	193·4	30·3	69	27	4
Omental ,,	193·3	33·6	66	29	5
Mesenteric ,,	192·6	33·1	65	31	4

All these fats are thus probably very similar in quantitative composition to the reindeer fat.[54]

It is apparent from Table 30A that, whilst all the fats there recorded include something approaching 30 per cent. of palmitic acid in their component acids, the amount of stearic acid may be almost as high or considerably less. The three fats quoted in Table 30B contain comparatively small proportions of stearic acid, and correspondingly more oleic acid, but the content of palmitic acid still approaches 30 per cent., and the oleic acid present is accompanied by relatively small amounts of polyethenoid acids.

The chief value at present of the figures in Table 30B is the hint which they afford of further interesting data awaiting collection in this field. The kangaroo fat examined by Maddison [21] is almost indistinguishable from those of our common herbivorous cattle (*v. infra*), although it comes from a marsupial widely removed from the latter both by evolutionary development and by environmental conditions. On the other hand, the panda fat seems to be set apart by its higher content of octadecadienoic acids, much of which is the linoleic acid of seed fats and not the ill-defined isomerides which make up the small quantity of this group present in ox or sheep fats (*v. infra*); the panda is remarkable as an ancestrally carnivorous animal which has become wholly herbivorous, its food being almost exclusively the bamboo.

The Ceylon sloth bear, similarly, is a member of the bear family whose natural diet is for the most part herbivorous—largely fruits supplemented by honey and sometimes insects (especially white ants), young birds and eggs. The specimen from which the fat was taken was fed in captivity on mice and sugar with occasional meat. The body fat component acids were similar in nature to most of the others in Tables 30A and 30B, except for an unusally large content of hexadecenoic acid. The fat was reminiscent in this respect of the body fats of rats fed on high carbohydrate or protein diets (*cf.* Longenecker,[44] p. 80).

Depot fats of sheep and oxen (tallows). The analyses of these products, quoted in Table 31, are based upon materials from industrial sources, i.e. on marketed specimens of authentic sheep or ox fats and not on fats taken from specific parts of a single animal or group of animals. They represent bulked samples of depot fats from many animals and may have been derived from back, abdominal, or perinephric (suet) fats, or a mixture of all of these. Most of the available detailed analyses (performed wholly or in part by the modern ester-fractionation procedure) are included in Table 31, but the most recent figures, in which account has been taken of the minor components, hexadecenoic and unsaturated C_{20} acids, are given separately in Table 32.

TABLE 31. *COMPONENT ACIDS (WTS. PER CENT.) OF DEPOT FATS OF SHEEP AND OXEN (MUTTON AND BEEF TALLOWS)*

(ANALYSES NOT INCLUDING HEXADECENOIC ACID OR UNSATURATED C_{20} ACIDS)

	SATURATED			UNSATURATED	
	C_{14}	C_{16}	C_{18}	OLEIC	"LINOLEIC" *
Sheep (*Ovis aries*)—					
South American [58]	1	21	30	43	5
Australian [58]	2	25	23	47	3
Australian [59]	4	25	31	36	4
Ox (*Bos taurus*)—					
North American [58]	2	32·5	14·5	48	3
North American [60]	6·3	27·4	14·1	49·6	2·5
South American [58]	2·5	25	20	47·5	5
South American [60]	4·5	30·6	19·2	42·7	3·0
South American [60]	7·8	27·8	24·4	38·9	1·1
South American [60]	5·8	24·0	28·6	41·6	—
Australian [58]	2	26·5	22·5	49	—

* The "linoleic" acid of these depot fats is better termed octadecadienoic acid (or acids), since it differs from that of vegetable fats in failing to yield a tetrabromo-adduct of m.p. 114°, and only yields traces of the tetrahydroxystearic acids, m.p. 155° and m.p. 173°, on oxidation with alkaline permanganate (*vide infra*, p. 89).

The figures in Table 31 only include myristic and "linoleic" acids as minor components. More recent study has demonstrated the presence in ox depot fats of small proportions of several other acids, which amount together (including myristic acid) to about 6–8 per cent. of the total fatty acids. In 1934 Brown and Sheldon [61] showed that traces of unsaturated C_{20} (arachidonic) acid are present in beef tallows; Brown and Deck [61] had previously observed (1930) the presence of about 0·4 per cent. of this acid in pig body fats. Again, intensive examination of cow milk fats had resulted (*cf.* pp. 113, 116) in establishing the presence of small amounts of mono-ethenoid acids containing fewer than 18 carbon atoms in the molecule, and had also led to the conclusion that ordinary linoleic acid (yielding a tetrabromostearic acid, m.p. 114°) was present, if at all, only in minute quantities (the diethenoid C_{18} acids present being apparently other geometrical isomerides of $\Delta^{9,12}$-octadecadienoic acid). Hilditch and Longenecker [62] therefore reinvestigated the component acids of three ox depot fats (portions of the perinephric (suet) fats from, respectively, a 7-year-old Shorthorn cow (I), a 4-year-old Shorthorn bullock (II), and a 3-year-old Shorthorn heifer (III) reared on Berkshire farms), employing a more delicate fractionation column than those used in the earlier work.

They demonstrated the presence of the following minor component acids:

(*a*) Traces of a saturated acid (? lauric) of lower molecular weight than myristic acid.

(*b*) Traces of a saturated acid (arachidic) of higher molecular weight than stearic acid.

(*c*) Small amounts of Δ^9-tetradecenoic and Δ^9-hexadecenoic acids the latter amounting to about 2–3 per cent. of the total acids (the structure of the acids was proved by disruptive oxidation).

(*d*) The diethenoid C_{18} acids were shown to resemble those of cow milk fat (p. 116) in that, whilst disruptive oxidation yielded *n*-hexanoic and azelaic acids, addition of bromine yielded none of the tetrabromostearic acid, m.p. 114°, characteristic of linoleic acid, and oxidation with alkaline permanganate gave only traces of the tetrahydroxystearic acids, m.p. 155° and 173°.

(*e*) Traces of highly unsaturated C_{20} acids.

The full fatty acid compositions of the above three ox perinephric fats,[62] together with a further instance of an English ox perinephric fat (Hilditch and Paul [63]), and also the component acids of fat from the interior cavities of English ox bones (Hilditch and Murti [64a]) are given in Table 32 (*a*).

Corresponding data for some Indian ox depot fats [64b] (some of which present somewhat abnormal features) and for an Indian buffalo depot fat [124] are quoted in Table 32 (*b*).

Finally, detailed data for sheep depot fats [65] (Table 32 (*c*)) include figures for the component acids of perinephric and external tissue fats of a group of ewes grown at Cambridge on a standard diet to different live weights, and of fat ewes after fasting for different periods; whilst an analysis of external (rump) fat from a Somali sheep [21] is appended.

TABLE 32. *COMPONENT ACIDS (WTS. PER CENT.) OF OX AND SHEEP DEPOT GLYCERIDES (INCLUDING ALL MINOR COMPONENT ACIDS)*

(*a*) *English Ox Depot Fats*

Acid	Perinephric [62] I	Perinephric [62] II	Perinephric [62] III	Perinephric [63]	Bone Marrow [64a]
Lauric	—	0·2	0·1	0·5	0·1
Myristic	3·0	3·1	2·0	2·7	2·6
Palmitic	29·2	24·9	26·9	30·4	32·3
Stearic	21·0	24·1	26·5	23·7	15·5
Arachidic	0·4	0·8	1·3	—	—
Tetradecenoic	0·6	0·4	0·4	0·4	0·7
Hexadecenoic	2·7	2·4	1·9	1·7	3·0
Oleic	41·1	41·8	39·1	38·6	43·2
Octadecadienoic	1·8	1·8	1·7	2·0	2·6
C_{20-22} unsaturated	0·2	0·5	0·1	—	—

(*b*) *Indian Ox and Buffalo Depot Fats (mainly perinephric)*

	Calicut [64b] (cow)	Calcutta [64b]	Bombay [64b] (bullock)	Bombay [64b] (cow)	Buffalo [124]
Lauric	0·3	0·2	0·2	0·1	—
Myristic	3·1	2·4	3·7	4·5	3·3
Palmitic	32·9	36·9	37·1	41·4	31·5
Stearic	29·3	26·8	29·4	24·3	33·2
Arachidic	—	0·4	1·2	0·5	0·6
Tetradecenoic	0·4	0·3	0·4	0·4	0·3
Hexadecenoic	1·5	2·1	1·0	1·3	1·9
Oleic	30·7	29·2	25·9	26·4	28·9
Octadecadienoic	1·3	0·9	0·9	1·0	—
C_{20-22} unsaturated	0·5	0·9	0·2	0·1	0·3

(c) Sheep (ewes) on controlled diets [65]

	PERINEPHRIC FATS			EXTERNAL TISSUE FATS		
	(i) Feeding on "supermaintenance" ration					
Days on ration :	22	58	81	22	58	81
Live weight (lb.) :	91	127	151	91	127	151
Lauric	—	—	—	0·4	0·6	0·9
Myristic	2·9	2·7	2·3	3·4	3·0	3·1
Palmitic	24·0	24·7	26·2	27·8	28·0	28·3
Stearic	24·9	28·3	27·1	14·7	16·2	13·5
Tetradecenoic	0·7	0·3	0·3	0·4	0·3	0·2
Hexadecenoic	2·4	0·9	1·0	1·6	0·8	0·6
Oleic	39·2	36·8	38·7	46·3	46·6	50·8
Octadecadienoic	5·2	5·7	3·3	4·8	3·9	1·9
C_{20-22} unsaturated	0·7	0·6	1·1	0·6	0·6	0·7
	(ii) Fat ewes fasted					
Days fasted :	0	100	209	0	100	209
Live weight (lb.) :	148	113	72	148	113	72
Lauric	0·1	0·1	—	0·7	0·6	0·3
Myristic	1·7	3·0	2·8	1·9	2·2	3·7
Palmitic	26·8	23·6	23·0	33·9	30·5	24·3
Stearic	30·1	31·7	37·8	15·3	20·1	24·6
Tetradecenoic	0·2	0·2	0·2	0·3	0·3	0·3
Hexadecenoic	0·9	1·3	1·0	0·9	1·2	0·7
Oleic	34·8	35·4	32·1	41·2	41·4	44·1
Octadecadienoic	4·3	3·9	2·2	4·9	2·8	1·5
C_{20-22} unsaturated	1·1	0·8	0·9	0·9	0·9	0·5

The external tissue (rump) fat of a Somali or "fat-tailed" sheep, fed in the Colombo Zoo for about seven years, chiefly on greenstuff with concentrates (probably mainly coconut cake), did not differ greatly from the above in its component acids [21] :—myristic 2·2, palmitic 23·0, stearic 14·9 ; tetradecenoic 0·3, hexadecenoic 2·5, oleic 55·7 octadecadienoic 0·8 and C_{20-22} unsaturated 0·6 per cent. (wt.). The oleic acid content is several per cent. higher, and the palmitic acid content a few units per cent. lower, than the corresponding ewe fats (above), whilst diethenoid C_{18} acids are almost absent.

Banks and Hilditch [60] pointed out in 1931 that, expressed on a molar percentage basis, nine out of the ten sheep and ox depot fats quoted in Table 31 fell into two groups : in one group the component acids consisted of about 70 per cent. (mol.) of C_{18} acids with about 30 per cent. (mol.) of palmitic (with myristic) acid, whilst in the other the respective proportions were about 62 per cent. of C_{18} acids and about 38 per cent. of palmitic (with myristic) acid—the molar contents of stearic acid meanwhile varying from 13 to 29 per cent. They thus reached the conclusion that the characteristic feature of these fats is the presence of a more or less constant proportion of palmitic acid—in the neighbourhood of 30 per cent. (mol.) * of the total fatty acids ; the rest of the fat is made up substantially of C_{18} acids, so that the difference between a more saturated and a less saturated tallow is due essentially to varying proportions in the stearic and oleic acid contents, the combined amounts of these being, however, approximately constant. When we come to consider the distinctive glyceride structure of these animal depot fats (Chapter VII, pp. 304, 320) it will be seen that this feature in the component acids is accompanied by a characteristic relationship in the amounts present in these depot fats of fully saturated glycerides, which become unusually large as the content of stearic acid in the total fatty acids becomes considerable.

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* In these fats the molar percentages of palmitic acid are 1·5–1·8 units per cent. higher than the weight percentages given in Tables 31 and 32.

Recalculation of the ester-fractionation data of Banks and Hilditch[60] to allow for the presence of hexadecenoic acid gives figures which are of the same order as those obtained by Hilditch and Longenecker,[62] and in addition the apparent existence of two groups (*cf.* above) of ox and sheep depot fat component acids largely disappears. The latter investigators sum up the present position as follows:

> "From our present results and those of the earlier analyses, therefore, we incline to the view that the constancy of the C_{18} acids at about 60–65 per cent. (mol.) of the total fatty acids of tallow is even more marked than was at first thought, any increase in stearic acid being closely balanced by diminution of oleic acid. At the same time, and largely independently of the amount of unsaturated acids present, the palmitic acid content of nearly all tallows which have been analysed lies within the relatively constant limits of 30 (±3) per cent. (mol.)."

Several other points of interest arise from the detailed component acid analyses in Table 32:

(i) *Content of palmitic acid.* The characteristic content may vary somewhat according to the animal species. Thus the value of 30 (±3) per cent. (mol.) which is normally observed in ox depot fats appears to be slightly higher than that noted in the twelve ewe depot fats (28·5±4 per cent. mol.).

In certain of the Indian ox depot fats which were exceptionally low in oleic acid, the stearic acid content did not increase beyond about 28 per cent. (mol.) of the total fatty acids, and in these instances the extra saturated acid over and above this proportion was palmitic; the content of palmitic acid in such cases therefore exceeded considerably the normal figure of 30 per cent. (mol.), reaching in one example as much as 43 per cent. (mol.) Such ox depot fats appear, however, to be exceptional in this respect, their low degree of unsaturation being probably dependent primarily on the tropical conditions in which the animals in question were reared.

(ii) *Content of stearic acid.*—This is somewhat variable in both ox and sheep depot fats. In each group (as also in pig depot fats, pp. 93–96) the perinephric fats are more saturated than the external tissue fats, thus containing more stearic and less oleic glycerides than the latter. This variation is usually considered to be associated with the local body temperature of the animal at the site of the fat deposits (*cf.* pig fats, p. 96). As already mentioned, however, there are indications of a limit (at about 30 per cent. (mol.) of the total acids) beyond which the content of stearic acid in the component acids of a sheep or ox depot fat rarely rises.

The reciprocal nature of the stearic and oleic acid contents of these fats has an important bearing on their glyceride structure and upon the possible mechanism by which depot glycerides of varying composition (i.e., relative degree of unsaturation) may originate from a common stock of mixed palmito-oleo glycerides (*cf.* Chapter VII, p. 305).

(iii) *Minor component acids.* The proportions in which these are present appear to be specific to a great extent for each kind of animal.

Thus, of saturated acids, the content of myristic acid is much the same (2–3 per cent.) for both ox and sheep depot fats, but arachidic acid was not detected in any of the latter, although it is usually found in very small amounts (0·5–1 per cent.) in ox depot fats.

In the unsaturated series, hexadecenoic acid, which usually forms 2–3 per cent. of ox depot fat component acids, only forms about 1 per cent. of of the total fatty acids in sheep depot fats ; in the fats of both animals it is accompanied by traces of tetradecenoic acid. Unsaturated acids of the C_{20} and C_{22} series occur to the extent of about 1 per cent. in sheep fats, but definitely less than this (*nil*–0·5 per cent.) in ox body fats.

Perhaps the polyethenoid C_{18} acids (mainly octadecadienoic acids) are the most characteristic minor components, forming 4 (±1) per cent. of the acids in sheep depot fats, but only about 1–2 per cent. in ox depot fats. In both cases these acids are distinct from ordinary or seed fat linoleic acid, although traces of the latter are frequently also present. These depot fats thus resemble cow milk fats and many animal liver fats in the specific nature of the octadecadienoic acid or acids present.

(iv) *Fat synthesised by sheep.* Comparison of the (small) weight of fat in the controlled diet of the ewes whose fats are illustrated in Table 32 (*c*) (*i*), with the depot fats in the animals when killed shows that the greater part of the latter must have been produced by synthesis from carbohydrate or protein (*cf.* pig fats, Table 34A and p. 98). The increases in each component acid in the perinephric and external tissue fats between the ewe killed at 22 days and that killed at 81 days were approximately as follows :

	PERINEPHRIC		EXTERNAL	
	Weight (g.)	Molar ratio	Weight (g.)	Molar ratio
Lauric	—	—	39	1·3
Myristic	40	2·7	128	3·7
Palmitic	465	28·1	1182	30·0
Stearic	482	26·3	559	12·8
Tetradecenoic	5	0·3	8	0·2
Hexadecenoic	16	1·0	22	0·6
Oleic	684	37·5	2132	49·2
Octadecadienoic	56	3·1	71	1·6
C_{20-22} unsaturated	20	1·0	29	0·6

Of the three major component acids, the perinephric and external tissue fats respectively show relative increases of 1 mol. palmitic acid to 2·28 and 2·07 mols. of combined stearic and oleic acids, suggesting that palmitodi-C_{18}-glycerides are the main types of fat synthesised by the animal.

The more elaborate study of fats from pigs raised on a low fat diet (Table 34A and p. 98) led to a similar result, and also permitted conclusions to be drawn as to which acyl radicals were synthesised by the animal and which were derived by direct assimilation.

(v) *Utilisation of sheep depot fats.* The data given in Table 32 (*c*) (*ii*) for ewes during fasting suggest that little selective removal of fatty acids takes place during mobilisation of the depot fats, especially the perinephric fat. To a slight extent, however, palmitic glycerides seem to be a little more readily removed from the perinephric fat, and still more so in the case of the fat of the external tissues. The effect is in any case only small, but it is curious that in pig fats (*cf.* p. 98) an opposite tendency has been observed, i.e., tendency to remove oleic glycerides in preference to those of saturated acids. It should be remembered that, since all these depot fats consist of mixed glycerides (mainly palmitodioleins and oleopalmitostearins), any tendency in favour of withdrawal of a particular fatty acid must be partly obscured by other acids present in the mixed glycerides being inevitably and concurrently involved.

(vi) *Bone marrow fats.* The detailed component acid analysis of an ox bone marrow fat[64a] given in Table 32 suggests practical identity in composition between the bone cavity fat and other depot fats of the ox. Earlier data, less complete in character, have been given by Nerking[66a] for the yellow and red marrow fats of ox bones, and by Eckart[66b]; their figures do not correspond very well with those in Table 32, whilst a more recent general survey by Schmidt-Nielsen and Espeli[66c] of bones of cattle, pigs and reindeer (containing 8–13 per cent. marrow with fat contents of 83–93 per cent.) covers a still wider range of composition:

BONE MARROW FATS

OBSERVER		COMPONENT ACIDS (PER CENT. WT.)			
		PALMITIC	STEARIC	OLEIC	" LINOLEIC "
Nerking[66a]	Ox marrow (yellow)	8	14	78	—
	Ox marrow (red)	16	36	48	—
Eckart[66b]	Ox bones	ca. 20	ca. 20	ca. 52	ca. 8
Schmidt-Nielsen and Espeli[66c]	Ox and pig bones	←—— 21–56 ——→		75–40	4
„ „[66d]	Reindeer bones	26·5	12·5	54	2

The reindeer bone-marrow fatty acids (which were determined by ester-fractionation and also contained 5 per cent. myristic acid) have a general resemblance to those recorded for the loin depot fat[56] of a reindeer.

Depot fats (lards) of pigs (fed on diets low in fat). The records for pig depot fats are at present more numerous than for any other of the land animals. As in the ox and sheep depot fats, many of the component acid analyses (Table 33, p. 94) do not take account of all the minor components (notably hexadecenoic acid); these older data embrace the following groups of investigations:

(i) Hogs of varying age fed on rations low in fat (Ellis and Zeller[67a]).
(ii) Hogs fed on brewers' rice or on corn (Ellis and Isbell[67b]).
(iii) Outer back, inner back and perinephric fats of young pigs (Bhattacharya and Hilditch[68a]).
(iv) Outer back, inner back and perinephric fats of a sow (Banks and Hilditch[68b]).
(v) Back fats at varying depths from the skin of a sow (Dean and Hilditch[68c]).

Subsequently, a number of analyses of pig depot fatty acids have been made,[69a] employing an electrically heated and specially packed fractionating column in the distillations of the unsaturated esters; some of these results are quoted in Table 34A.* The depot fats in question were from pigs reared on diets † low in fat by Dr. Hammond at the Animal Nutrition

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* This work was carried out on behalf of the Food Investigation Board of the Department of Scientific and Industrial Research.

† DETAILS OF DIET:
From weaning to 16 *weeks.*—
High plane ration. One gallon separated milk per pig daily, with *ad lib.* meal mixture No. 1 (20 per cent. dried separated milk, 30 per cent. white fish meal, 30 per cent. middlings, 20 per cent. flaked meal).
Low plane ration. Half gallon separated milk per pig daily, with restricted ration of meal mixture No. 1.
From 16 *weeks onwards.*—
High plane ration. One gallon separated milk per pig daily, with *ad lib.* meal mixture No. 2 (30 per cent. white fish meal, 30

Research Institute of the School of Agriculture, Cambridge; the animals were fed on a "high" or a "low" ration to a final live weight of 200 lbs., and in certain cases the "high" ration was changed to "low," or *vice versa*, when the pigs were sixteen weeks old.

TABLE 33. *COMPONENT ACIDS (WTS. PER CENT.) OF PIG DEPOT FATS (LOW FAT DIETS) (ANALYSES NOT INCLUDING HEXADECENOIC ACID)*

	FAT	SATURATED			UNSATURATED		
	IOD. VAL.	C_{14}	C_{16}	C_{18}	OLEIC	"LINOLEIC"	C_{20-22}
(i) Hogs (composite body fats) of varying age:[67a]							
AGE (DAYS)							
110	61·2	1·2	25·6	8·5	58·1	6·6	—
134	57·4	0·8	27·9	9·0	57·7	4·6	—
246	53·3	1·1	26·1	11·5	60·5	0·8	—
257	55·1	0·8	25·4	11·0	61·5	1·3	—
(ii) Hogs fed on:[67b]							
Brewers' rice, etc. (Back fat)	52·6	1·8	26·4	12·1	58·5	1·2	—
Corn, etc. (Meat fat)	58·8	0·7	25·2	12·7	54·4	7·0	—
(iii) * Young pigs:[68a]							
Back, outer layer	62·6	2·0	24·6	10·6	53·3	9·5	—
,, inner ,,	55·0	1·4	29·6	13·9	47·2	7·9	—
Perinephric	45·7	3·6	28·5	21·4	41·3	5·2	—
(iv) † Back and perinephric fats of a sow:[68b]							
Back, outer, shoulder end	76·9	4·4	18·5	5·5	54·2	15·3	2·1
,, ,, central portion	72·6	3·8	20·3	7·9	54·1	13·0	0·9
,, ,, tail end	72·0	4·3	22·2	7·3	49·2	15·3	1·7
,, inner, shoulder end	71·1	4·2	22·8	8·6	47·5	15·6	1·3
,, ,, central portion	64·6	3·8	26·0	11·0	44·1	13·6	1·5
,, ,, tail end	64·6	4·3	23·3	13·8	43·5	13·9	1·2
Perinephric	59·0	3·9	27·7	17·6	35·7	13·7	1·4
(v) ‡ Back fats (varying depths) of a sow:[68c]							
Back, outer, central, outer layer	70·4	2·6	23·8	10·1	46·3	15·2	2·0
,, ,, ,, inner ,,	67·4	2·8	23·5	13·0	43·0	15·6	2·1
,, inner, ,, outer ,,	62·9	2·9	24·9	14·5	42·7	13·9	1·1
,, ,, ,, middle ,,	63·0	2·8	25·5	14·5	41·3	14·5	1·4
,, ,, ,, inner ,,	62·8	3·0	24·6	14·5	42·8	13·7	1·4

* Diet estimated to contain 1·5 per cent. of fat and 12 per cent. of protein
† Diet included a small proportion of fish-meal.
‡ Diet included no fish-meal.

In considering the figures in Tables 33 and 34A, the following points must be borne in mind:

(*a*) The data in Table 34A may be taken as the most comprehensive analyses available at present.

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per cent. barley meal, 30 per cent. flaked meal, 10 per cent. middlings).

Low plane ration. Half gallon separated milk per pig daily, with restricted ration of meal mixture No. 2.

Fat content of meal mixtures:

CONSTITUENT	MEAL	FAT (PER CENT.)	IODINE VALUE OF FAT
Dried separated milk	No. 1	1·0	42·5
White fish meal	Nos. 1 and 2	1·6	169·5
Wheat middlings	Nos. 1 and 2	4·1	116·0
Flaked maize	Nos. 1 and 2	1·3	114·6
Barley meal	No. 2	3·1	117·2

TABLE 34A. *COMPONENT ACIDS (WTS. PER CENT.) OF PIG DEPOT FATS (LOW FAT DIETS)*[69a] *(INCLUDING ALL MINOR COMPONENT ACIDS)*

	RATION		FAT	SATURATED			UNSATURATED				
	TO 16 WEEKS	AFTER 16 WEEKS	IOD. VAL.	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	OLEIC	" LIN-OLEIC "	C_{20-22}
(i) 16-*weeks-old animals.*—											
Gilt, outer back fat	" High "	—	57·2	1·0*	29·8	12·7	0·2	3·5	47·8	3·1	1·9
Gilt " " "	" Low "	—	58·3	1·3	28·1	11·8	Trace	4·8	42·9	8·2	2·9
(ii) *Animals reared to* 200 *lbs. live weight.*—											
Gilt, outer back fat	" Low "	" Low "	65·5	0·8*	25·9	12·2	0·2	2·0	48·1	7·8	3·0
Hog " " "	" Low "	" High "	55·9	1·1*	28·2	13·5	0·2	2·4	47·0	5·2	2·4
Hog " " "	" High "	" Low "	58·8	0·7	25·3	13·1	0·1	2·0	51·0	5·3	2·5
Gilt " " "	" High "	" High "	60·0	1·3	28·3	11·9	0·2	2·7	47·5	6·0	2·1
Gilt, inner " "	" High "	" High "	54·3	1·0	30·1	16·2	0·3	2·7	40·9	7·1	1·7

* Traces of a lower saturated acid (probably lauric) are included in the myristic figure.

(*b*) The figures in Table 33, (iii), (iv), and (v) have been calculated, in the cases of the fractionally distilled " liquid " or mainly unsaturated esters, as though only unsaturated C_{18} esters and esters of palmitic and myristic acids were present, no allowance being made for hexadecenoic esters. Consequently the apparent contents of myristic acid are higher than the true values by nearly 3 per cent., whilst the palmitic acid figures are probably about 1 per cent. below the true values.

(*c*) The data in Table 33, (i) and (ii), are derived from ester-fractionation of the *saturated* acids, whilst the unsaturated acids are derived merely from the iodine values of the " liquid " acids. Hence the figures for myristic and palmitic acids may be slightly low (no allowance having been made for the small quantities of these acids passing into the " liquid " acids), and also the proportions of linoleic acid may actually be somewhat higher than recorded.

When due allowance is made for these minor variations in the analytical procedures used in the analyses recorded in Tables 33 and 34A, it is clear that, with pigs reared on diets relatively low in fat, the major component depot fatty acids are palmitic, stearic, and unsaturated C_{18} acids (in which oleic acid predominates). Out of every 100 mols. of fatty acids, approximately 30 (or slightly less) are those of palmitic acid (the molar percentage of palmitic acid in these fats is 1·5–1·8 units per cent. more than the weight percentages recorded in the tables). Similarly, the combined molar content of C_{18} acids is in nearly all cases between 65 and 70 per cent. of the total fatty acids. As in ox and sheep depot fats, but to a somewhat less degree, the proportions of stearic acid are variable. In the cases of fats from different depots of the same animal (Table 33, (iii), (iv), (v)) it is also evident that the combined percentages of stearic and oleic acids are approximately constant, i.e. increase in stearic acid is mainly at the expense of oleic acid, or *vice versa*. These relationships will receive further consideration in connection with the glyceride structure of pig depot fats (Chapter VII, pp. 304, 320).

Concurrently with these general approximations to constancy in palmitic and total C_{18} acid contents, it will be noticed that the most unsaturated fats usually also contain somewhat less palmitic acid than usual. This is especially noticeable in the outer layers of back fat at the extreme ends (especially the shoulder) of this layer of adipose tissue.

The outer layers of the back fat of pigs are somewhat more unsaturated in character (higher oleic acid content) than the inner layers, whilst the perinephric fat of the animal is still more saturated and contains the greatest content of stearic acid. Henriques and Hansen[70] concluded that the determining factor here was the temperature of the site of the fat deposits in the animal (e.g. back of pig: 1 cm. deep, 33·7° C.; 4 cm. deep, 39·0° C.; rectum, 39·9° C.), and obtained further support for this hypothesis by maintaining three pigs from the same litter at different temperatures—one at 30–35°, one at 0°, and one at 0° but covered with a sheepskin coat; the iodine values of the outermost layers of the back fats from these animals, after the two months, were respectively 69·4, 72·3, and 67·0. The detailed analyses of Dean and Hilditch[68c] (Table 33, (v)) afford general confirmation of Henriques and Hansen's views, but suggest that the increase in softness (i.e. unsaturation) is confined to the outermost layer of the outer back fat. The inner part of the outer layer, and the inner back fat (i.e. the portion beneath the " streak ") which forms the greater part of the whole of the back fat are almost homogeneous in composition throughout.

It is noticeable that, in many of the outer back fats which have been analysed, the stearic acid content is close to 12–13 per cent. (wt.) ; in the inner back fats this usually rises by about 4 units per cent.

The proportions of " linoleic " acid also merit attention. In the first place it may be pointed out that the octadecadienoic acids of pig depot fat usually yield, on treatment with bromine, fair amounts of the tetrabromostearic acid, m.p. 114° ; whilst alkaline permanganate oxidation gives the two tetrahydroxystearic acids, m.p. 157° and 173°, characteristic of the linoleic acid of seed fats (*cf.* Chapter IX, p. 421). In this respect the octadecadienoic acids of pig depot fat therefore differ appreciably from the depot and milk fats of oxen. The amounts of " linoleic " acid recorded in different cases vary widely, from 1 per cent. (or probably somewhat more) in young hogs (Ellis *et al.*[67a, b]) to 14–15 per cent. in the case of sows several years old.[68b, c] In the latter cases it is evident that the high linoleic acid is approximately constant as compared with the differing oleic and stearic acid contents of fats from different sites in the same animal. This suggests that linoleic acid may be derived by direct ingestion from the small amounts of vegetable fats in the diets, and that possibly it may not be so readily released or mobilised from the depots as oleic, palmitic, and stearic acids. The data on fats from animals during starvation offer further elucidation of this point (Table 34B).

Of the minor component acids, it may be pointed out that small traces of lauric and of tetradecenoic acid are probably usually present. Myristic acid only amounts to about 1 per cent. of the total acids, whilst Δ^9-hexadecenoic acid appears to be fairly constant at about 2–3 per cent. (wt.).

The case of the highly unsaturated acids of the C_{20} and C_{22} series is less certain and perhaps more variable. Brown and Deck,[61] depending on the yield of ether-insoluble polybromo-additive products from the total depot fatty acids of the pig, recorded only 0·4 per cent., but fractionation analyses reveal the presence of 1–3 per cent. How far this depends on, for example, the ingestion of fish meal fatty acids is uncertain. This might well account for the presence of these acids in the fats recorded in Table 33 (iv) and Table 34A, but so far as could be ascertained the animal to which the analyses in Table 33 (v) refer had received no fish meal in its diet. The source of these highly unsaturated minor components of pig depot fat therefore awaits the results of further investigation. De la Mare and Shorland,[72a] working with ester fractions from 415 grams of a pig back fat, concentrated and refractionated the esters of the C_{20} and C_{22} acids, which formed 1·4 per cent. of the total fatty acids. The content of highly unsaturated acids (estimated from insoluble polybromo-adducts) did not exceed, however, 0·4 per cent., and the remaining 1 per cent. appeared to be a mixture of di- and monoethenoid C_{20} acids.

The pigs, from which the fats illustrated in Table 34A were derived, were reared on known diets and a complete record of the total weights of fat in each animal was available. Consequently it was possible to prepare a balance sheet of the weight of each fatty acid ingested as fat by the experimental animals, and, within approximate limits, of the weight of each fatty acid deposited as fat in the animal when it had reached 200 lb. live weight. The results were uniform for each of the four animals in Table 34A (ii), and may be illustrated by that fed on the " Low-High " rations :

FATTY ACIDS	IN DIET (kg.)	DEPOSITED (kg.)	DIFFERENCE (kg.)
Saturated :			
Below C_{14}	0·11	Trace	−0·11
Myristic	0·24	0·29	+0·05
Palmitic	1·28	8·27	+6·99
Stearic	0·25	3·99	+3·74
Unsaturated :			
C_{16} (and C_{14})	0·22	0·89	+0·67
Oleic	3·24	13·87	+10·63
Linoleic	3·30	1·48	−1·82
C_{20-22}	0·87	0·74	−0·13
	9·51	29·53	+20·02

The greater part of the palmitic, stearic, oleic, and hexa- (with tetra-) decenoic acids have clearly been produced by the animal from carbohydrate (or protein) food. The small amount of myristic acid is of the same order as that in the ingested fats, and the evidence as to its origin is thus inconclusive.

Saturated acids of lower molecular weight than myristic acid are neither synthesised nor laid down from dietary fat by the pig. The quantity of linoleic acid in the pig body fats is less than half of that available in the food, suggesting that, like the rat, the pig is not able to synthesise linoleic acid. This is further supported by the fact that the octadecadienoic acid of pig fats, unlike those of ox or sheep depot fats, is to a large degree seed fat linoleic acid. The quantity of unsaturated C_{20-22} acids in the pig depots likewise falls short of that present in the diet (as fish-meal constituents) ; but the disparity is less pronounced than in the case of linoleic acid, and it is possible that some of these acids are synthesised by the animal, perhaps from linoleic acid (*cf.* Nunn and Smedley-MacLean [50]). The observed variations in the content of these C_{20-22} acids can often be correlated with the amount of fish meal in the feed, and thus they are evidently assimilated therefrom to a definite extent ; but the nature of the deposited acids [61, 69a, 72] differs from that of the corresponding fish oil acids, and selective absorption of some of the latter group may be involved.

Of the three main fatty acid products of synthesis—palmitic, stearic and oleic—it is of interest to note that the ratio of increase of palmitic to the two C_{18} acids, in the four outer back fats (Table 34A (ii)), was 1 : 1·86, 1 : 2·06, 1 : 2·18 and 1 : 2·50 (wt.). The mean ratio for the four animals was 1 : 2·08 (wt.) or 1 : 1·89 (mol.), i.e. close to that demanded by predominant synthesis of palmitodi-C_{18}-glycerides from carbohydrate in the animal (*cf.* sheep depot fats, p. 92).

Other pigs which had been reared to 200 lbs. live weight on the controlled diet * were subsequently starved for different periods, during which they would, of course, be dependent to a large extent on their depot fat as source of energy. The alteration in the composition of their depot fats during inanition is shown by the data in Table 34B (Hilditch and Pedelty [69b]).

Apart from minor differences, there is no great evidence of selectivity in mobilisation of any one fatty acid component of depot fats during starvation of the pig. The most prominent subsidiary effects are preferential removal of oleic acid during the later stages of inanition, and definite reluctance in the earlier stages to mobilise those acids (linoleic and unsaturated

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* *Cf.* footnotes, p. 93.

TABLE 34B. *COMPONENT ACIDS (WTS. PER CENT.) OF DEPOT FATS OF PIGS DURING STARVATION*

FAT	DAYS FASTED	FAT IOD. VAL.	SATURATED				UNSATURATED				
			C_{12}	C_{14}	C_{1}	C_{18}	C_{14}	C_{16}	OLEIC	"LINOLEIC"	C_{20-22}
Perinephric	0	56·4	—	0·9	29·3	17·4	0·3	1·8	40·3	8·1	1·9
,,	51	56·6	0·1	0·8	31·3	17·6	0·1	1·0	38·8	8·3	2·0
,,	135	54·8	—	0·9	30·3	21·5	0·2	2·2	34·1	7·3	3·5
Inner back	0	58·9	0·1	0·8	27·5	15·1	0·2	1·7	44·2	7·3	3·1
,, ,,	51	59·9	—	0·6	29·4	15·0	0·2	2·4	40·0	9·6	2·8
,, ,,	135	54·7	0·1	0·9	30·7	18·8	0·2	1·7	37·2	7·1	3·3
Outer back	0	63·9	0·1	0·9	26·5	12·8	0·2	1·9	46·8	7·9	2·9
,, ,,	51	65·0	—	0·9	26·0	13·0	0·2	1·7	45·6	9·1	3·5
,, ,,	135	60·0	—	0·9	30·1	15·1	0·2	2·6	39·5	8·2	3·4

C_{20-22} acids) which are derived from ingested dietary fats. These findings, however, differ from observations on sheep during inanition, where palmitoglycerides seemed to be mobilised slightly more readily than the rest (p. 92).

It seems well to emphasise that the problem of fat mobilisation cannot be satisfactorily discussed in terms of the fatty acids—the various mixed glycerides in which these occur clearly have a profound bearing on the process. Thus, the most abundant glycerides in pig depot fats are palmitodioleins and oleopalmitostearins. If oleic acid is selectively desired, it must be found in molecules of these types. Similarly, a minor component acid, such as linoleic or unsaturated C_{20-22} acids, will in general contribute only one group to a triglyceride molecule, the others being oleic, or oleic and palmitic. Hence a molecule of linoleodiolein, for example, might be attacked, as it were, for the sake of its oleic groups, although the linoleic group is somewhat less readily amenable to utilisation.

The problem of fat mobilisation is, in fact, fundamentally one from which considerations of glyceride structure cannot be excluded.

Attention is directed to two further papers in which Shorland and de la Mare [72b] discuss in considerable detail the effect of skim milk and buttermilk diets, supplemented in some cases with maize meal or copra, upon the component acids of pig back fats, and the relation between the growth rate of the animals and the composition of their body fats. Linoleic acid is more readily assimilated and deposited by slow-growing, and lauric and myristic acids by fast-growing pigs. The authors conclude, however, that the composition of the fat in different parts of animals in general is probably mainly determined by the depot and species, and is not readily altered by dietary changes.

Depot fats of pigs fed on diets which included various fats. The changes brought about in the reserve fats of animals as a result of the presence of specific fats in the diet have received special notice in the case of the pig, chiefly as the result of the studies of Ellis and his colleagues.

The figures (Table 33 (i)) given by Ellis and Zeller [67a] for the component acids present in the composite body fats of hogs of varying age and weight, fed on a diet low in fat, together with those of Ellis and Isbell [67b] (Table 33 (ii) and Table 35, below), serve as a basis of comparison with their further analyses of fats from pigs whose diet included various kinds of added fats. Ellis and Isbell [67b] studied the influence of ingested fats on the composition of the pig body fats in a somewhat drastic manner by feeding different animals from the same litter on (*a*) brewer's rice, tankage, and grass; (*b*) maize, skim milk, and grass; (*c*) soya beans alone; and (*d*) groundnuts alone. The balanced diets (*a*) and (*b*) contained not more than 5 per cent. of vegetable fat, whereas (*c*) and (*d*) must have contained from 20 to 40 per cent. of the vegetable fats specific to soya beans and groundnuts respectively. The fatty acids in the various body fats were found to be composed as shown in Table 35:

TABLE 35. *COMPONENT ACIDS (WTS. PER CENT.) OF DEPOT FATS OF PIGS FED ON SOYA BEANS OR GROUNDNUTS*

Feed	Fat		Component Fatty Acids (Per Cent.)						
			Saturated				Unsaturated		
	From	Iod. Val.	C_{14}	C_{16}	C_{18}	C_{20}	Oleic	Linoleic	Linolenic
(*a*) Brewer's rice, etc.	Back	52·6	1·8	26·4	12·1	—	58·5	1·2	—
(*b*) Corn, etc.	Meat	58·8	0·7	25·2	12·7	—	54·4	7·0	—
(*c*) Soya beans alone	Back	90·7	0·7	17·3	9·5	—	40·4	31·9	0·2
(*c*) ,, ,, ,,	Back	100·6	0·3	14·1	7·9	—	38·9	38·3	0·5
(*d*) Groundnuts alone	Meat	84·1	0·4	15·5	7·5	0·2	56·9	19·5	—
(*d*) ,, ,,	Meat	91·8	0·1	10·4	4·9	0·3	64·6	19·7	—

This remarkable series shows that, whilst a balanced diet containing not more than 5 per cent. of vegetable fat leads to body fats of exactly the same type as those given in the previous table, a ration of vegetable seeds alone leads to the following effects: (*a*) considerable diminution in the proportion of palmitic acid and the complete breakdown of the normal, approximately constant amount of the C_{18} acids as a whole (*cf.* p. 96), (*b*) increase in the linoleic acid to proportions approaching those in the ingested vegetable fats, and (*c*) failure to produce stearic acid even to the normal proportion observed in pigs fed on an ordinary balanced diet. Moreover, acids (respectively linolenic and arachidic in soya bean and groundnut oils) present in the vegetable fats in minor amounts appeared in the animal body fats as a result of this intensive vegetable seed diet.

The precise concentration of added fat in the diet beyond which the normal composition of the body fat is definitely altered is indicated by a further series of experiments by Ellis, Rothwell, and Pool,[71] in which pigs were fed on a basal diet (hominy, tankage, alfalfa meal, and mineral mixture, containing less than 1 per cent. fat), supplemented by varying amounts of cottonseed oil, with the results shown in Table 36.

TABLE 36. *COMPOSITE BACK FATS OF HOGS FED ON VARYING RATIONS OF COTTONSEED OIL*

Feed	Fat	Component Fatty Acids (Per Cent.)				
	Iod. Val.	Myristic	Palmitic	Stearic	Oleic	Linoleic
Basal diet alone	60·6	1·7	25·5	13·7	50·2	8·9
,, ,, +4 per cent. C.S.O.	60·5	1·1	25·0	21·1	39·5	13·3
,, ,, +8 per cent. C.S.O.	64·4	0·8	21·9	23·3	35·8	18·2
,, ,, +12 per cent. C.S.O.	77·4	1·1	13·8	26·5	31·8	26·8

At some point between 4 and 8 per cent. of added fat in the diet, the total C_{18} acid content ceases to be approximately constant and commences to rise considerably, while the proportion of palmitic acid, of course, falls correspondingly. This is an especially good illustration of the fact that excessive fat in the diet cannot be dealt with by an animal in the same way as the fat which it itself normally produces; the palmitic acid content of the body fat of the hogs fed on a diet containing 12 per cent. of cottonseed oil was less than that of the cottonseed oil itself (component acids of cottonseed oil: myristic 0·5, palmitic 22, stearic 2, oleic 30·5, linoleic 45 per cent.).

It is also observable that, with increasing proportions of cottonseed oil in the diet, the stearic acid content of the body fats was likewise augmented; whereas, in the cases of the pigs fed on soya beans or groundnuts alone, the stearic acid in the body fat declined below the normal figure. This suggests that the animals in the cottonseed oil experiments were able to elaborate, from the 88 per cent. or more of basal diet which was always present, a certain amount of stearic acid (at the expense of oleic acid) in order partially to compensate for the increasing quantities of assimilated linoleic acid.

The studies of Ellis and his co-workers appear to contain material which goes far to explain the various factors which determine the extent to which assimilated fat can be utilised by the pig (and probably by other animals) for the purpose of its own reserve fat. In addition, we may mention that Brown[61] has found that lard from pigs fed on a diet which included 14 per cent. of menhaden oil contained 2·7 per cent. of C_{20} and C_{22} acids, which were slightly less unsaturated than the corresponding acids of the menhaden oil; Brown and Deck[61] had previously pointed out that pig body fats normally contain very small amounts (up to 0·4 per cent.) of the acids in question.

Influence of dietary fat on depot fat of other animals. As regards tallows, it is generally accepted that the higher melting point and more saturated nature of beef tallows from South America and Australia as compared with the softer North American tallows is to be connected with the diet; in the first-named areas the cattle are practically entirely grass-fed, while in North America the practice is to fatten them to a large extent on oil-cakes (cottonseed, maize, linseed) rich in unsaturated glycerides. On the other hand, Thomas, Culbertson, and Beard[73] found that liberal allowances of whole soya beans, menhaden oil, corn oil or coconut oil fed to steer calves for 260 days had no perceptible effect on the unsaturation of their body fats. It may therefore be that different species of animals differ in the extent to which they utilise ingested fats in their reserve fats. (That oxen may be exceptional in this respect is further suggested by the observation that linoleic, linolenic, or erucic glycerides, fed to cows in the forms of linseed oil or rape oil (*cf.* pp. 119–122), do not pass to any marked extent into the milk fat glycerides.)

Horses fed continuously on grass or green fodder lay down fat very similar to mutton or beef tallow, whereas the fat of a horse when corn-fed is more oily and of a lower melting point.

Experiments on dogs by Lebedev and by Munk led to similar results many years ago. In one instance,[74a] two dogs were first starved and then fed, one on linseed oil and the other on mutton tallow; the reserve fat of the first did not solidify at 0°, whereas that of the second melted at about 50°. Similarly, a dog fed with rape oil laid down adipose tissue fat in which erucin was detected.[74b]

From the above it will be fairly clear that animals can, and indeed do normally, provide adequate supplies of reserve fats mainly by synthesis from carbohydrates or other components of their diet; but that, in addition, they can utilise for this purpose the fatty acids present in the form of vegetable fats in their food. In view of the specifically constant nature of the various reserve fats deposited by animals which have lived on a diet containing only normal, relatively small proportions of fat, and of the manner in which the normal composition of their reserve fats is changed by ingestion of unusually large proportions of fat in the food, it seems reasonable to conclude that the most natural, and therefore probably the most healthy, condition is for animals to synthesise, rather than to assimilate directly, the greater part of their own reserve fats.

DEPOT FATS OF THE CARNIVORA AND OMNIVORA

As mentioned earlier, data in this field are still very scanty. Amongst the few detailed analyses so far made are those of body fats from a lion, cat, and baboon which lived in the Colombo Zoological Gardens (Hilditch and Sime[21]). The lion had been fed chiefly on beef, supplemented with liver ; the diet of the cat, obviously flesh, was not known in detail ; the baboon had been fed mainly on boiled rice and fruit, but in the wild state this species eats chiefly insects, small animals, fruits, berries and roots. The component acids of the three body fats are given in Table 37A.

TABLE 37A. *COMPONENT ACIDS (WTS. PER CENT.) OF BODY FATS OF LION, PUMA, TIGER, CAT, AND BABOON*

	LION[21] (*Panthera leo*) BODY	PUMA[75d] (*Felix concolor*) BODY	TIGER[75e] (*Felix tigeris*) BODY	CAT[21] (*Felix catus*) BODY	SACRED OR DOG-FACED BABOON[21] (*Papio hamadryas*) ABDOMINAL
Decanoic	1·4	—	—	—	—
Lauric	1·1	—	—	2·4	—
Myristic	4·9	1·3	1·3	3·6	3·2
Palmitic	28·9	22·4	12·8	29·2	18·9
Stearic	17·8	26·9	26·8	16·6	5·8
Arachidic	0·1	3·7	5·0	—	—
Tetradecenoic	0·6	—	—	1·2	0·8
Hexadecenoic	1·9	12·6	—	4·3	3·8
Oleic	40·3	26·2	54·1 *	40·8	53·8
Octadecadienoic	—	2·3	—	1·9	13·2
C_{20-22} unsaturated	3·0	4·6	—	Trace	0·5

* Minor unsaturated acids not given.

The lion and cat fats are almost identical in composition with the mainly synthesised depot fats of the herbivorous ox or sheep (Table 32). This may reasonably be due to the circumstance that all these fats are produced in the animals either from carbohydrate, or from protein (probably via carbohydrate). The very small proportions of saturated acids of lower molecular weight than myristic acid may not be significant, since they may well have been derived at second-hand, so to speak, from the flesh of animals which had fed on coconut cake at Colombo.

The Mexican puma (*F. concolor*) is carnivorous, but feeds chiefly on herbivorous mammals, especially young deer and sheep. Giral[75d] remarks that the high stearic acid content is similar to that found in sheep and similar body fats. The high proportion of hexadecenoic acid is unusual and recalls that of Ceylon bear fat (p. 86, Table 30B), and of rats fed on very high carbohydrate or protein diets (p. 79, Table 28B).

The fat of the sacred baboon, the food of which (like that of the Ceylon bear, Table 30B, p. 86) was probably mainly or wholly vegetable and not animal in character, presents certain special features: the low content of palmitic acid and the high content of octadecadienoic acid (which was in fact mainly ordinary or seed fat linoleic acid). The proportion of palmitic acid (20 per cent. mol.) is much below that usually characteristic of land animal body fats. Whether this is due to the presence of assimilated vegetable fats (as suggested by the presence of 13 per cent. of vegetable linoleic acid), or whether it is a species characteristic of the Primates, remains to be seen (*cf.* below, human body fats). The linoleic acid, which evidently contributes to the unusually high octadecadienoic acid figure of the baboon fat, probably derives from assimilated dietary vegetable fat.

Three other wild animal fats contained the usual small proportions of hexadecenoic acid and other minor component acids.

Partial data (saturated and unsaturated acids) have been recorded for only two other wild animal fats, although scattered records of saponification and iodine values exist for the depot fats of a few other animals. The figures quoted refer to the back and hindquarters fats of the American black bear, *Ursus americanus* (Hoyt [75a]) and the body fat of the mink, *Putorius lutreula* (Lode [75b]):

	SATURATED Per Cent. (wt.)	UNSATURATED Per Cent. (wt.)
American black bear [75a]		
Back	16	84
Hindquarters	33	67
Mink [75b]	33	67

The saturated acids of the mink fat were probably about 30 per cent. palmitic and 3 per cent. stearic; some of the unsaturated acids were apparently of higher molecular weight than C_{18}.

Rasmussen *et al.*[75c] have described the subcutaneous fat of a very obese female American black bear killed in Ontario in 1942, but calculated its component acids only from lead salt separation, iodine and thiocyanogen values (saturated 11·5, oleic 70, linoleic 12 and linolenic 6·5 per cent.). *Ursus americanus*, like the Ceylon sloth bear, is almost exclusively herbivorous in its food, but of course the analytical methods utilised [75a, 75c] do not serve to indicate whether hexadecenoic acid was present in the black bear fat, or indeed the real proportions of any of the individual component acids therein.

Human depot fats. Until recently, except for a few iodine values and similar general characteristics, there has been little information in regard to the component acids of depot fats of human beings; but in 1943 Cramer and Brown [76] recorded data, based on ester fractionation coupled with low-temperature crystallisation, for five body fats from middle-aged and elderly persons who had died from pathological conditions (*e.g.*, arteriosclerosis, cardiac hypertrophy, etc.) not likely to be of significance in the history of the depot fats. The component acids of these fats, which were mainly abdominal, mesenteric or perirenal, are quoted in Table 37B.

The saturated acids are the usual mixture, with relatively low stearic acid (as in the baboon); the palmitic acid content is a few per cent. lower than the 28–30 per cent. met with in many animal fats, but the difference is not great. (A similarly somewhat reduced palmitic acid content appears to characterise human milk fat as compared with cow milk fat, *cf.* p. 129.)

TABLE 37B. *COMPONENT ACIDS (WTS. PER CENT.) OF HUMAN BODY FATS*[76]

	Female 53 Yrs.	Male 74 Yrs.	Male 61 Yrs.	Male 66 Yrs.	History unknown
Lauric	0·1	0·6	—	0·9	—
Myristic	2·7	5·9	2·6	3·9	2·6
Palmitic	24·0	25·0	24·7	25·7	25·4
Stearic	8·4	5·8	7·7	5·2	7·7
Tetradecenoic	0·2	0·6	0·4	0·5	0·4
Hexadecenoic	5·0	6·7	7·3	7·6	5·6
Oleic	46·9	45·4	45·8	46·6	44·8
Octadecadienoic	10·2	8·2	10·0	8·7	11·0
C_{20-22} unsaturated	2·5	1·8	1·5	0·9	2·5

The unsaturated acids are distinguished by the facts that oleic acid forms nearly half of the total fatty acids and that ordinary linoleic acid is present in abundance in the 8–11 per cent. of octadecadienoic acids. Isomeric forms of both octadecenoic and octadecadienoic acid were, however, shown also to be present in the human body fat. The hexadecenoic acid (which occurs in somewhat more than the usual proportion for a land animal body fat) was shown to be the Δ^9-acid which has been observed throughout the realm of natural fats. In the C_{20-22} unsaturated acids (also slightly above the normal proportion) arachidonic acid was present in some quantity.

The similarity of human body fat to the depot fats of many other land animals, especially in its contents of oleic and of palmitic acid, appears to be established by the above analyses.

ANIMAL DEPOT FATS—SUMMARY

The characteristic composition of the fatty acids in the depot fats of different species of animal, and the usual range of variations in the component acids of depot fats of one and the same species of animal, have been dealt with at some length in the preceding pages. It seems desirable, in concluding this section, to focus attention on the varying types of depot fat which have been considered by a table which includes examples, from the most detailed analyses available, of all the classes which have come under review. Table 38 (p. 105) therefore includes a selection of the data referred to in the previous pages; obviously it cannot take account of all the variations encountered within a single species, although two more or less extreme cases are quoted for both ox and pig depot fats. The object of Table 38 is to illustrate the variations in depot fatty acid compositions as between one class of animal and another, rather than to give a complete picture of the range of fatty acid compositions within the depot fats of any given species. Since possible species variations in the body fats are under consideration, the illustrations are confined to animals known to have received diets low in fat or, at least, their natural food (in which fat forms as a rule but a small proportion, say up to 5 per cent., of the whole diet).

TABLE 38. *TYPICAL COMPONENT ACIDS (WTS. PER CENT.) OF THE DEPOT FATS OF DIFFERENT CLASSES OF ANIMAL*

CLASS	ANIMAL	DEPOT FAT	IOD. VAL.	SATURATED				UNSATURATED			
				C_{14}	C_{16}	C_{18}	C_{20}	C_{16}	OLEIC	OCTADECA-DIENOIC	C_{20-22}
Amphibian	Frog [12a]		120	4	11	3	—	15	52		15
Reptile	Tortoise [12b]		87	1	14	4	—	9	65		7
,,	Lizard [12b]		76	4	18	7	—	10	56		5
,,	,, [13]		70·8	4	29	10	—	12	40		5
Bird	Domestic hen [20]	Abdominal	79·7	0·6	25·4	4·2	—	7·1	43·0	18·4	1·3
,,	Grey goose [21]	,,	57·1	8·2 *	20·3	5·6	—	2·5	41·6	6·6	2·3
,,	Emu [21]	Subcutaneous	65·8	0·9	17·5	10·1	0·6	2·1	62·2	5·2	0·5
Rodent	Rat [41]	Body	57·3	4·5	28	2	—	7	58·5	—	—
,,	,, [42]	,,	59·7	5·6	29·3	2·5	—	14·0	48·6	—	—
,,	,, [44]	,,	62·5	3·1	26·7	3·6	0·4	15·6	47·2	2·2	0·3
Herbivora	Horse [52]	Abdominal	82·7	—	28	5	—	—	50	13	—
,,	Pig [69a]	Back, outer	60·0	1·3	28·3	11·9	—	2·7	47·5	6·0	2·1
,,	,, [69a]	Back, inner	54·3	1·0	30·1	16·2	—	2·7	40·9	7·1	1·7
,,	Ox [62]	Perinephric	43·2	3·0	29·2	21·0	0·4	2·7	41·1	1·8	0·2
,,	Reindeer [54]	Loin	33·7	7	35	20	1	—	37	—	—
,,	Sheep [59]	Perinephric	41·2	4	25	31	—	—	36	4	—
,,	,, [65]	,,	43·4	2·7	24·7	28·3	—	0·9	36·8	5·7	0·6
,,	,, [65]	External	49·1	3·0	28·0	16·2	—	0·8	46·6	3·9	0·6
,,	,, Somali [21]	Rump	49·0	2·2	23·0	14·9	—	2·5	55·7	0·8	0·6
,,	Goat [56]	Back	33·5	2·1	25·5	28·1	2·4	—	38·4	—	—
,,	Kangaroo [21]	Body	50·1	4·7	25·5	14·1	1·5	2·7	45·5	2·6	2·8
,,	Giant panda [21]	Abdominal	64·8	5·0	26·4	6·7	—	3·6	45·1	11·9	—
Omnivora	Ceylon (sloth) bear [21]	Body	60·3	2·6	28·7	3·4	—	10·6	50·5	1·0	1·8
,,	Sacred baboon [21]	Abdominal	77·0	3·2	18·9	5·8	—	3·8	53·8	13·2	0·5
,,	Human [76]	Male, 74 years	67·4	5·9	25·0	5·8	—	6·7	45·4	8·2	1·8
,,	,, [76]	Female, 53 years	68·9	2·7	24·0	8·4	—	5·0	46·9	10·2	2·5
Carnivora	Cat [21]	Body	43·6	3·6	29·2	16·6	—	4·3	40·8	1·9	—
,,	Lion [21]	,,	41·0	4·9	28·9	17·8	0·1	1·9	40·3	—	3·0

* Also 12·3 per cent. lauric acid.

Hexadecenoic acid was not allowed for in the analyses of horse, reindeer, sheep,[59] and goat depot fats, and unsaturated C_{20-22} acids were similarly not determined in these cases and in the rat depot fats *ref. nos.* 41 and 42.

Component Acids of the Lipids (Glycerides and Phosphatides) of Animal Organs

A certain amount of detailed information has appeared in recent years with reference to the component acids present in the lipids of various animal organs, especially the liver. In contrast to adipose tissue fats, which consist almost wholly of glycerides, and in which phosphatides are only present, if at all, in minute traces, the lipids of animal organs include both glycerides and phosphatides in important proportions. Fortunately, in a number of recent analyses, the glycerides and phosphatides have been separated from each other as completely as possible by taking advantage of the sparing solubility of the latter in acetone, and separate studies have thus been carried out on the respective component acids of the glyceridic and phosphatidic fractions.

LIVER LIPIDS

(a) *Liver Glycerides*

So far as can be traced, detailed analytical data by the ester-fractionation procedure are available for the mixed fatty acids of the liver glycerides of the frog, Greek tortoise, pig, ox, and sheep. These are collected in Table 39. It should be observed that, owing to the sparing solubility of mono-oleo-disaturated glycerides in cold acetone, the separation of glycerides and phosphatides by this solvent is probably not quite complete ; on the other hand, the amount of such glycerides present in liver lipids will be relatively small, and the error thereby introduced will correspondingly also be comparatively small. At the same time, the " glyceride " fraction of the liver lipids includes any free fatty acids present in the liver, and also any fatty acids present in combination with cholesterol. The amount of the latter is relatively small (1–3 per cent. of the glyceride fraction), but the free fatty acids present are variable and range, in Hilditch and Shorland's observations,[77a] from about 10 to 50 per cent. of the glyceride fractions of the liver lipids.

TABLE 39. *COMPONENT ACIDS (WTS. PER CENT.) OF ANIMAL LIVER GLYCERIDES*

CLASS	ANIMAL	SATURATED				UNSATURATED				
		C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Amphibian	Frog [12a]	19–23 per cent. (mainly palmitic)				—	61		16–20	
Reptile	Greek tortoise [12b]	1	11	4	—	—	15	66 (−2·1H)	3 (−4·5H)	
Herbivora	Pig [77a]	0·1	22·5	9·5	—	—	8·9	47·0 (−2·4H)	10·6 (−6·8H)	1·4 (−6·8H)
,,	Ox [77b]	—	25	20	—	—	9	37 (−2·6H)	8 (−5·0H to −7·5H)	1
,,	Ox [77a]	1·4	30·4	6·6	—	1·1	9·9	40·3 (−3·0H)	8·5 (−6·9H)	1·8 (−6·9H)
,,	* Cow [77a]	2·8	29·8	5·3	—	0·4	9·7	48·6 (−2·4H)	3·4 (−6·0H)	—
,,	Sheep [77a]	0·2	21·9	12·9	—	—	4·9	44·7 (−2·8H)	11·6 (−7·3H)	3·8 (−7·8H)

* This specimen of liver exhibited marked fatty degeneration.

Comparison of Tables 39 (liver glycerides) and 38 (depot glycerides) reveals some interesting features. In the first place, the content of palmitic acid in both groups of glycerides is approximately the same in each animal species; in the liver glycerides, as in the depot fats, the palmitic acid content rises from a figure reminiscent of marine animal fats (in the amphibia and reptiles) until it approaches 25-30 per cent. (in the liver glycerides of oxen); the corresponding figure for sheep and pig liver glycerides seems to be slightly lower (22 per cent.). Apart from this, the liver glycerides only resemble the corresponding depot fats quantitatively in the content of unsaturated C_{18} acids (the mean unsaturation of which is, however, definitely higher than in the corresponding depot fat acids).

Qualitatively, the liver glycerides differ from those of the adipose tissues in the presence of much greater amounts of unsaturated C_{20} and C_{22} acids, and of hexadecenoic acid; and (in the larger land animals) of considerably less stearic acid. In the liver glycerides of pigs, oxen, and sheep, hexadecenoic acid forms, as a rule, about 9 per cent. of the total acids, whilst unsaturated acids of the C_{20} and C_{22} series (with a mean unsaturation equivalent to between 3 and 4 double bonds in the molecule) normally account for 10 per cent. or somewhat more of the total fatty acids. Stearic acid, on the other hand, although somewhat variable in proportion, is often much reduced in amount as compared with the corresponding depot fats.

The diethenoid C_{18} acids present in the liver, as in the depot, glycerides appear to be isomeric forms of ordinary or seed fat linoleic acid, since they do not yield more than small proportions of the tetrabromo- or tetrahydroxystearic acids characteristic of the latter.

Judged by the average composition of their component acids, therefore, the liver glycerides of all the higher land animals so far studied exhibit fundamental differences from the corresponding glycerides in their reserve fats, but resemble the latter in their total contents of unsaturated C_{18} acids and, especially, in the proportions of palmitic acid present. One is tempted to go further, and to suggest that, in the land animal group, the component acids of the liver glycerides bear considerable quantitative resemblance to each other, irrespective of the species; but with the restricted data available this conclusion must clearly be uncertain.

In the course of their studies of the absorption of ingested fats by rats, Channon, Jenkins, and Smith [47] found that the saturated acids of the rat liver glycerides closely resembled those of the carcass both in the proportion of the total fatty acids and in their mean molecular weights, while the unsaturated acids were less closely related.

In the instances available for amphibia and reptiles, it seems that there is, on the contrary, considerable resemblance between depot and liver glycerides.

(*b*) *Liver Phosphatides*

In Table 40 will be found component fatty acid analyses of liver phosphatides corresponding with those for the liver glycerides recorded in Table 39.

Table 40 (liver phosphatides) should be considered in close conjunction with Table 39 (liver glycerides) and Table 38 (depot glycerides). It is readily seen that the liver phosphatide component acids differ from those of the liver glycerides much more even than the latter do from those of the depot fats. Of the saturated acids, palmitic acid is definitely less prominent than in the other two classes of fats of pigs, oxen, and sheep, and usually (but not always) forms less than 15 per cent. of the total acids; stearic acid, on the other hand, is present in much greater proportions than in the liver glycerides, and in several cases exceeds the amount customarily found in the corresponding depot fats. In the unsaturated acids, those of the C_{18} series are usually somewhat more unsaturated than in the liver glycerides (and include little, if any, ordinary or " seed fat " linoleic acid), but form a somewhat lower proportion of the total acids; whilst hexadecenoic acid is also lower than in the liver glycerides, generally amounting to about one-half to two-thirds of its percentage in the latter (but in the case of the sheep liver examined by Hilditch and Shorland, the reverse condition was observed). Unsaturated C_{20} and C_{22} acids are present, however, in greater amounts than in the liver glycerides; in the pig, ox, and sheep phosphatides the combined proportions of this group are in the neighbourhood of 20 per cent. of the total fatty acids.

It is interesting to recall that, amongst fish fats, similar relationships have been noted between the phosphatides and glycerides present in the roe of the New Zealand ling and also in the liver of the groper (Chap. II, p. 52).

TABLE 40. *COMPONENT ACIDS (WTS. PER CENT.) OF ANIMAL LIVER PHOSPHATIDES*

CLASS	ANIMAL	SATURATED				UNSATURATED				
		C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Amphibian	Frog [12a]	25 per cent. (mainly palmitic)				—	42 per cent. (mainly C_{18})		33	
Reptile	Greek tortoise [12b]	—	15	10	—	—	10	48 (−2·8H)	17 (−6H)	
Herbivora	Pig [77a]	—	12·1	15·4	1·8	—	4·8	39·9 (−2·2H)	24·1 (−6·5H)	1·9 (−6·5H)
,,	Ox [78]	—	12	30	—	—	—	40 (−3·4H)	18 (−8H)	—
,,	Ox [77b]	—	12·5	27	—	—	5	27 (−3·0H)	18 (−5·3 to −8·2H)	10·5
,,	Ox [77a]	1·3	28·2	14·4	0·2	0·7	3·8	31·5 (−2·9H)	19·9 * (−7·5H)	
,,	† Cow [77a]	—	21·3	21·8	—	—	4·1	47·8 (−2·7H)	5·0 (−6·0H)	—
,,	Sheep [77a]	—	12·6	21·8	0·8	—	8·9	27·8 (−3·1H)	23·6 (−6·9H)	4·5 (−10·5H)

* Mainly C_{20}.
† This specimen of liver exhibited marked fatty degeneration.

The general result is that the component acids of liver phosphatides show a greater resemblance, irrespective of the animal species, than those of either of the other two groups. It is true, of course, that this resemblance is still by no means complete, but the extreme variations, so far as can be judged, in any one group from the frog to the ox, are much smaller than in the liver or depot glycerides.

In the pig, ox, and sheep, the general features of all three groups may be illustrated by Table 41 (p. 109), taken from Hilditch and Shorland's paper [77a];

the data are given in molar percentages, and those for the liver glycerides and phosphatides have been corrected to allow as far as possible for the imperfect separation of the two groups of lipids by differing solubility in acetone.

TABLE 41. *A COMPARISON OF THE CORRECTED FATTY ACID COMPOSITIONS OF THE NON-PHOSPHATIDE (" GLYCERIDE ") AND PHOSPHATIDE CONSTITUENTS OF THE OX, COW, PIG, AND SHEEP LIPIDS WITH THE AVAILABLE DATA FOR THE CORRESPONDING DEPOT FATS. FATTY ACIDS (PER CENT. MOL.)*

	SATURATED				UNSATURATED				
	C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Ox liver:									
" Glyceride "	1·6	32·5	5·0	—	1·5 (−2·0H)	11·7 (−2·0H)	40·3 (−3·0H)	7·4 * (−6·9H)	
Phosphatide	1·5	29·7	17·0	0·2	0·6 (−2·0H)	1·6 (−2·0H)	27·7 (−2·9H)	21·7 * (−7·5H)	
Depot glyceride ‡	7·3	29·2	20·5	—	—	—	43·0 (−2·1H)	—†	—
Cow liver:									
" Glyceride "	3·2	34·7	5·3	—	0·5 (−2·0H)	9·9 (−2·0H)	43·6 (−2·4H)	2·9 (−6·0H)	—
Phosphatide		22·9	21·2	—	—	4·4 (−2·0H)	46·9 (−2·7H)	4·6 (−6·0H)	—
Pig liver:									
" Glyceride "	0·1	25·8	10·3	0·2	—	9·2 (−2·0H)	44·1 (−2·4H)	9·2 (−6·8H)	1·1 (−6·8H)
Phosphatide	—	13·4	15·3	1·7	—	5·3 (−2·0H)	40·3 (−2·2H)	22·4 (−6·5H)	1·6 (−6·5H)
Depot glyceride §	1·1	28·1	9·7	—	—	—	61·1 (−2·1H)	—†	—
Sheep liver:									
" Glyceride "	0·3	24·2	12·5	—	—	5·3 (−2·0H)	44·1 (−2·8H)	10·5 (−7·3H)	3·2 (−7·8H)
Phosphatide	—	13·9	21·7	0·7	—	9·9 (−2·0H)	28·0 (−3·1H)	21·9 (−6·9H)	3·9 (−10·5H)
Depot glyceride ‖	2·1	24·6	25·6	—	—	—	47·7 (−2·2H)	—†	—

* Mainly C_{20}.
† Traces of C_{20} acids are also present in these depot glycerides.
‡ Mean values—Banks and Hilditch;[60] *cf.* Armstrong and Allan.[58]
§ Mean values—Ellis and Zeller;[67a] *cf.* Ellis and Isbell,[67b] Bhattacharya and Hilditch.[68a]
‖ Mean values—Armstrong and Allan,[58] *cf.* Collin *et al.*[59]

The differences in the relative proportions of palmitic, stearic, hexadecenoic, unsaturated C_{18}, and unsaturated C_{20} and C_{22} acids in the three groups are highly significant, and may be commended to the consideration of those who appear at times, perhaps, too ready to assume that organ and depot fats must be, if not nearly related, at all events closely derivable from each other by actions involving, as a rule, merely addition or removal of hydrogen. They indicate conclusively that each acid must be considered, very largely, independently of the others in any explanation which may ultimately be offered of their location in the respective fats of the higher land animals. It may be helpful therefore, in illustration of this point, to give a tabular statement (based on the data in Tables 38, 39, and 40) which offers a general summary of the distribution of these individual acids:

ACID	DEPOT GLYCERIDES	LIVER GLYCERIDES	LIVER PHOSPHATIDES
Palmitic	High	High	Lower
Stearic (variable)	High	Low	High
Hexadecenoic	Very low	Higher	Medium
C_{18} unsaturated	High	High	Lower
C_{20} and C_{22} unsaturated	Very low	Medium	High

This comparison refers, of course, to the cases of pigs, oxen, and sheep. At the other end of the scale the data are not so detailed, and the amount of saturated acids in all three groups of lipids is lower ; but here also the proportion of unsaturated C_{20} and C_{22} acids is much increased, and that of the unsaturated C_{18} acids decreased, in the liver phosphatides as compared with the liver or depot glycerides.

In the case of the rat, Channon, Jenkins, and Smith[47] also observed that the liver phosphatide acids showed no relationship with the carcass fatty acids.

LIPIDS OF OTHER ANIMAL ORGANS

The fats of few animal organs, other than the liver, have yet been investigated in detail, but figures for individual component acids are available in the case of the lipids of the heart-muscle and adrenals of the ox. Broadly speaking, these analyses suggest closer resemblance to those of the liver glycerides or phosphatides than to those of depot glycerides. Unsaturated C_{20} (and C_{22}) acids are prominent in each case, whilst the palmitic contents are lower than in the depot glycerides ; hexadecenoic acid was probably not allowed for in most of these studies. The data in question are collected in Table 42.

TABLE 42. *COMPONENT FATTY ACIDS (WTS. PER CENT.) OF THE LIPIDS FROM VARIOUS PARTS OF THE OX*

			SATURATED				UNSATURATED			
LIPIDS OF		OBSERVERS	C_{14}	C_{16}	C_{18}	C_{20}	C_{16}	C_{18}	C_{20}	C_{22}
Heart-muscle	Glycerides	Klenk and Ditt[77c]	—	22	20	—	12	45	—	—
	Phosphatides	,, ,,	—	14	21	—	—	45	14	1
Adrenals	Phosphatides	Ault and Brown[79]	1·2	23·8	11·1	2·0	—	40·2	22·2	—

One of the very few studies yet made of human organ lipids is that of the non-phosphatidic fraction of the fatty matter in atheromatous internal tissues of the aorta. McArthur[80] has found that the component acids of these mixed glycerides and cholesterol esters included palmitic 14·6, stearic 2·9, oleic and octadecadienoic 74·6, arachidonic 2·1, and acids insoluble in light petroleum (? possibly higher saturated acids) 5·8 per cent. (wt.). Apparently the oleic acid content was about 45 per cent., and 9·4 per cent. of the total fatty acids was isolated in the form of the tetrabromostearic acid (m.p. 114°) corresponding to linoleic acid.

The kidney tissues of the cat have been reported by Turner[81] to contain lipid matter in which, in addition to the more usual fatty acids, saturated acids apparently of the C_{14} and C_{16} group, which are liquid at the ordinary temperature, are present. Fatty acids of this kind have not yet been noted in other animal organ lipids, although they occur in certain animal waxes, e.g. that of sheep's wool, and in some glandular secretions such as that of the ear.

OX BLOOD LIPIDS

Certain studies of the lipids of ox blood have been made which may ultimately prove of importance in tracing the passage of glycerides from the liver or other organ to the sites where they are deposited. Parry and Smith [82] made an examination of the component acids from the total mixed lipids in ox blood which suggested the presence of palmitic 10, stearic 13, arachidic 3, oleic 20, linoleic 6, C_{20} unsaturated 33 and C_{22} unsaturated 10 per cent. (wt.).

Kelsey and Longenecker [83] made a very comprehensive survey of the fatty matter in blood drawn from 6 Holstein cows which had been fed on hay and water during the 24 hours prior to the blood collection. 90 litres of cow blood furnished 42 litres of plasma from which was obtained 109 gms. of lipids. These consisted of:

	Per cent. (*wt.*)
Free fatty acids	19·9
Glycerides	16·9
Cholesterol esters	46·0
Phosphatides	17·2

The component acids of the first three groups were determined by ester fractionation with the following results (per cent. mol.):

	FREE FATTY ACIDS	GLYCERIDES	CHOLESTEROL ESTERS
Myristic	0·8	0·2	—
Palmitic	34·4	33·7	11·1
Stearic	5·2	22·2	3·3
Arachidic	2·7	0·5	0·3
Hexadecenoic	—	2·6	4·2
Oleic	40·5	21·3	7·9
Linoleic	16·4	18·4	61·7
Linolenic	—	—	9·2
Arachidonic	—	1·1	2·2

The acids of the cholesterol esters stand apart in their low saturated content and their very high proportion of linoleic (with some linolenic) acid. Significantly, the octadecadienoic acids in each group seemed to be almost wholly seed fat linoleic acid.

The blood glyceride figures are of great apparent interest in regard to the question of the origin of depot and milk fats (*cf.* this chapter, pp. 91, 117, and Chapter VII, pp. 304–310). Here again the C_{18} unsaturated acids, although of similar total proportion to those in cow depot fats, contained large proportions of the ordinary "linoleic" acid which is almost wholly absent from the depot and milk fats. In contrast, the saturated acids of the blood glycerides show almost exact quantitative resemblance to those of the more saturated types of ox or cow depot fat.

It is clearly needful for studies of this kind to be pursued and extended.

Component Acids of Animal Milk Fats

The component fatty acids of some milk fats, especially, perhaps, those of herbivorous mammals, differ from those of either the depot or organ fats of the same animal by including, in addition to palmitic, stearic, oleic, and linoleic acids, definite but small proportions of butyric, caproic, caprylic, capric and lauric acids, with a somewhat larger amount of myristic acid than is present in the depot fats. Naturally, most of the detailed component acid analyses of milk fats are those of cow milk fats, although a few data are available for the milk fats of other herbivora—buffalo, sheep, goat, and camel.

Before discussing these figures it should be pointed out that the component acids of other mammalian milk fats undoubtedly show wide variations in their proportions of lower saturated acids. Probably the 4 per cent. (weight) of butyric acid in cow milk fatty acids approaches the maximum amount present in any milk fat. At the other end of the scale we have the milk fats of marine mammals such as the whale, which have been shown by Schmidt-Nielsen and Frog [84a] and by Klem [84b] to contain no acids of lower molecular weight than those present in whale depot or liver fats, and whose component acids are quantitatively closely similar to those of the depot fats (*cf.* Chapter II, p. 56). It is therefore more or less an open question as to which species of mammals are characterised by the production of definite proportions of lower saturated acids in their milk glycerides.

Some indication on this point is to be gained by comparing the average Reichert-Meissl and Polenske values of the milk fats of different animals. The Reichert-Meissl values, being measures of the water-soluble, steam-volatile fatty acids present in a fat, give comparative indications of the amounts of butyric and hexanoic (caproic) acids; the Polenske values, giving similar measures of the content of water-insoluble, steam-volatile fatty acids, afford similar comparative indications of the relative proportions of octanoic and decanoic (caprylic and capric) acids. Typical data for a number of milk fats are as follows:

Milk Fat	Reichert-Meissl Value	Polenske Value
Dog	1·2	
Pig	1·7	
Human	1·4–3·4	1·5–2·2
Mouse	2·9	
Cat	4·4	
Horse	7·0	6·1
Ass	13·1	
Rabbit	16·1	
Camel	16·4	1·6
Goat	20–29	3·2–9·8
Sheep	23–33	2·2–6·9
Buffalo	26–34	1·6–2·4
Cow	33–36	1·3–3·5

It is evident that the proportion, if any, of butyric or hexanoic acid in milk fats such as those of the dog, pig, or human being is very small, and that the presence of 3–4 per cent. of butyric acid is confined to a particular group of animals, of which the cow is the best known example.

Detailed analyses of milk fatty acids. These were among the first to be attempted by means of the ester-fractionation procedure but, as the necessity for prior separation of the steam-volatile components by distillation in steam, and of separation of the saturated and unsaturated higher fatty acids by means of lead salts, was not at the time fully appreciated, the earlier results obtained for milk fatty acids were divergent and far from accurate, Later on, however, a number of more definite results have been published. mainly for the component acids of cow milk fat, but also including those of some other herbivorous animals.

In addition to lower saturated acids, it has been established that minor proportions of Δ^9-mono-ethenoid acids containing 10, 12, 14, and 16 carbon atoms are also present in cow and other milk fats. The presence of a decenoic acid was first deduced in 1912 by Smedley,[85] and confirmed in 1922 by Grün and Wirth,[86] who isolated it and determined its structure. The presence of C_{12}, C_{14}, and C_{16} unsaturated acids was indicated in a later paper by Grün,[86] whilst in 1933 Bosworth and Brown [87] presented further evidence for decenoic and tetradecenoic acids but were unable to detect C_{12} or C_{16} unsaturated acids. In 1936 Riemenschneider and Ellis [88] found C_{10}, C_{14}, and C_{16} mono-ethenoid acids in goat milk fat ; in 1936–1937 Hilditch and Paul [89] and Longenecker [90] isolated C_{10}, C_{12}, C_{14}, and C_{16} mono-ethenoid acids from cow milk fat and showed that in each case they were Δ^9-unsaturated acids. The possible bearing of these observations on the mode of production of typical milk fat glycerides will receive consideration in later chapters (VII, p. 306; VIII, p. 356).

In many of the detailed analyses (Tables 43A, 44B and 45A) the presence of these minor proportions of lower unsaturated acids has not been taken into account, but in more recent publications (Tables 43B, 44A, 44C, 45B and 46) these have also been included. It is desirable, therefore, to record the respective data in separate tables. It is furthermore desirable to put on record the data for milk fat component acids in the form both of weight and of molar percentages. The wide variation in molecular weight of the component acids causes the latter to be quite different in some respects from the former. Weight percentages alone, therefore, do not present even an approximately accurate picture of the proportionate number of molecules of each fatty acid present.

Component acids of cow milk fats from pasture or stall-fed animals.— Analyses of the component acids of milk fats from a variety of stall and pasture-fed cows are illustrated in Tables 43A (minor unsaturated components not included) and 43B (fully detailed analyses). These cover cows at spring, summer and autumn pastures, or during winter feeding in the stall, when the diets of the Berkshire cows [89, 90, 97, 98] consisted of hay with roots, kale and small proportions of concentrates whilst that of the Cheshire cows [110] was entirely of ensiled green fodder * mixed with hay.

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* The silage was made from a mixture of first year grasses (25·3 per cent. each of S23 perennial ryegrass, Swedish evergreen perennial ryegrass, and smooth meadow grass, 7·6 per cent. each of crested dogstail, chewings fescue, and *Agrostis tenuis*, and 1·3 per cent. of Kentish wild white clover) dried under standard conditions, mixed with 48 lb. molasses per ton of dried fodder, and stored in a closed silo for five months.

TABLE 43A. *COMPONENT ACIDS OF COW MILK FATS (MINOR UNSATURATED COMPONENTS NOT INCLUDED)*

	New Zealand				Berkshire, England								
	Market Samples			Spring Pasture	Autumn Fed	Early Summer Pasture Fed	Stall Fed Winter	Stall and Pasture	Spring Pasture	Stall Fed Winter	Stall Fed Winter	Indian "Ghee"	
Acid	I[95]	II[95]	III[95]	1928[96]	1928[96]	1929[96]	1932[97]	1932[97]	1932[97]	1934[98]	1934[98]	I[94]	II[94]
				(i) *Weight Percentages*									
Butyric	3·1	3·4	3·2	3·5	3·1	3·3	3·9	3·3	3·1	4·4	4·4	3·3	2·6
n-Hexanoic	1·9	1·8	1·7	1·7	1·7	1·3	1·5	1·7	1·7	2·2	1·4	2·1	1·9
n-Octanoic	0·8	0·9	0·8	1·3	1·6	1·2	0·7	0·7	0·7	2·4	1·8	1·0	1·4
n-Decanoic	2·0	1·9	2·3	3·1	2·1	2·2	1·9	1·8	1·8	3·8	1·9	2·3	3·6
Lauric	3·9	3·1	4·3	4·1	3·4	4·0	3·7	2·3	3·2	4·4	3·1	3·7	5·7
Myristic	10·6	9·7	10·8	11·1	6·9	10·4	8·4	8·8	7·1	10·9	9·3	5·8	10·6
Palmitic	28·1	27·6	28·4	27·3	29·0	26·1	22·0	21·8	22·8	23·1	27·5	30·0	29·1
Stearic	8·5	12·2	9·4	11·5	7·6	6·5	15·0	12·7	12·5	12·6	12·2	11·2	6·7
as Arachidic	1·0	0·7	0·5	0·6	0·9	—	0·7	0·4	0·7	0·7	1·0	—	—
Oleic	36·4	34·3	33·2	31·3	40·1	40·9	38·5	40·7	41·3	28·9	33·1	35·5	34·0
as Octadecadienoic	3·7	4·4	5·4	4·5	3·6	4·1	3·7	5·8	5·1	5·6	3·1	5·1	4·4
as C_{20-22} unsaturated	—	—	—	—	—	—	—	—	—	1·0	1·2	—	—
				(ii) *Molar Percentages*									
Butyric	8·4	9·2	8·7	9·2	8·4	8·9	10·6	8·9	8·5	11·5	11·7	8·8	6·9
n-Hexanoic	3·9	3·7	3·4	3·4	3·5	2·7	3·2	3·5	3·5	4·3	2·8	4·2	4·0
n-Octanoic	1·3	1·4	1·4	2·2	2·7	2·0	1·2	1·2	1·2	3·7	2·9	1·6	2·2
n-Decanoic	2·8	2·7	3·1	4·2	2·9	3·0	2·6	2·6	2·6	5·0	2·6	3·2	4·9
Lauric	4·6	3·7	5·1	4·7	4·1	4·7	4·4	2·7	3·8	5·0	3·6	4·4	6·7
Myristic	11·0	10·2	11·2	11·5	7·2	10·9	8·8	9·4	7·5	10·8	9·5	6·1	10·9
Palmitic	26·2	25·7	26·3	25·0	27·1	24·3	20·5	20·6	21·6	20·5	25·2	27·9	26·8
Stearic	7·1	10·2	7·8	9·5	6·4	5·4	12·6	10·8	10·7	10·1	10·0	9·4	5·5
as Arachidic	0·8	0·5	0·6	0·5	0·7	—	0·5	0·3	0·6	0·5	0·8	—	—
Oleic	30·8	28·9	27·9	26·1	33·9	34·6	32·5	35·0	35·6	23·3	27·4	30·0	28·4
as Octadecadienoic	3·1	3·8	4·5	3·7	3·1	3·5	3·1	5·0	4·4	4·5	2·6	4·4	3·7
as C_{20-22} unsaturated	—	—	—	—	—	—	—	—	—	0·8	0·9	—	—

TABLE 43B. *COMPONENT ACIDS OF COW MILK FATS (MINOR UNSATURATED COMPONENTS INCLUDED)*

	Cow (Berkshire, England)		Cow (Cheshire, England)			Cow (U.S.A.)
	Stall-fed Winter 1935 [89]	Stall-fed Winter 1937 [90]	Silage-fed Winter 1940–41 [110a]	Early Summer 1941 [110a]	Late Summer 1941 [110a]	Colostrum Fat 1944 [128b]
Acid	(i) *Weight Percentages*					
Butyric	3·7	3·0	3·6	3·7	3·5	2·6
n-Hexanoic (caproic)	2·0	1·4	2·0	1·7	1·9	1·6
n-Octanoic (caprylic)	1·0	1·5	0·5	1·0	0·7	0·5
n-Decanoic (capric)	2·6	2·7	2·3	1·9	2·1	1·6
Lauric	1·7	3·7	2·5	2·8	1·9	3·2
Myristic	9·3	12·1	11·1	8·1	7·9	9·5
Palmitic	25·4	25·3	29·0	25·9	25·8	31·7
Stearic	10·7	9·2	9·2	11·2	12·7	11·8
as Arachidic	0·4	1·3	2·4	1·2	1·5	0·6
Δ^9-Decenoic	0·2	0·3	0·1	0·1	0·1	0·1
Δ^9-Dodecenoic	—	0·4	0·1	0·2	0·2	0·2
Δ^9-Tetradecenoic	1·2	1·6	0·9	0·6	0·6	0·7
Δ^9-Hexadecenoic	5·0	4·0	4·6	3·4	2·4	2·7
Oleic	32·4	29·6	26·7	32·8	34·0	28·5
as Octadecadienoic	4·0	3·6	3·6	3·7	3·7	2·5*
as C_{20-22} unsaturated	0·4	0·3	1·4	1·7	1·0	1·8
	(ii) *Molar Percentages*					
Butyric	9·8	8·1	9·5	9·9	9·5	7·2
n-Hexanoic	4·1	2·8	4·1	3·5	4·0	3·4
n-Octanoic	1·6	2·5	0·8	1·6	1·1	0·8
n-Decanoic	3·5	3·7	3·2	2·6	2·9	2·3
Lauric	2·0	4·4	2·9	3·4	2·3	3·9
Myristic	9·6	12·5	11·5	8·5	8·2	10·1
Palmitic	23·4	23·2	26·7	24·0	24·1	29·9
Stearic	8·9	7·6	7·6	9·4	10·7	10·0
as Arachidic	0·3	1·0	1·8	0·9	1·1	0·5
Δ^9-Decenoic	0·3	0·4	0·1	0·1	0·1	0·2
Δ^9-Dodecenoic	—	0·5	0·1	0·2	0·2	0·2
Δ^9-Tetradecenoic	1·3	1·7	0·9	0·6	0·7	0·7
Δ^9-Hexadecenoic	4·6	3·7	4·3	3·2	2·3	2·5
Oleic	27·0	24·8	22·4	27·7	28·8	24·3
as Octadecadienoic	3·3	2·9	3·1	3·1	3·2	2·2*
as C_{20-22} unsaturated	0·3	0·2	1·0	1·3	0·8	1·5

* Also octadecatrienoic acid 0·4 (wt.) or 0·3 (mol.).

Whilst the analyses in Table 43B must be regarded as the most comprehensive and the most accurate in detail, those in Table 43A conform to the more detailed analyses in all respects, save that the oleic acid figures are probably 3–5 per cent. too high (since they include unsaturation represented in reality by the small amounts of C_{10}, C_{12}, C_{14}, and C_{16} mono-ethenoid acids). The effect of this upon the figures for the saturated acids in Table 43A is small in any individual case, because the result of the inclusion of the various lower unsaturated acids with oleic acid is spread, as it were, over a number of the homologous saturated acids.

Taking the more prominent individual acids of milk fats (and basing comparisons on their molar proportions), it is seen that, as in the corresponding depot fats, *palmitic* and *oleic* are the chief component acids. The content of *palmitic acid* again has some approach towards constancy, but is somewhat lower than in the depot fats. The average figure is probably in the region of 24–26 per cent., rather than 30 per cent. Milk fats from individual cows examined over a range of some years by Dean and Hilditch [97] suggest that the proportion of palmitic acid in the milk fat declines with progressive age of the lactating animal.

The proportions of *oleic acid* are likewise lower in the milk fats than in the depot fats of cows, and show a similar behaviour in that, the amount of palmitic acid being roughly constant, there is a reciprocal relation between the proportion of oleic acid and that of the saturated acids, especially stearic acid. These relations are not so well defined as in the depot fats, and this is natural since the composition of milk fat is more liable to variation in consequence of seasonal and other causes. This is most marked, perhaps, in the sudden change which occurs when the cattle pass from winter stall feeding to graze on early spring or summer pasture. This results in a sudden increase of about 3 to 6 units in the iodine value of the milk fat and a less marked decline in its Reichert-Meissl value (which is subsequently re-established). Some influence connected with the seasonal change causes an increase of a few per cent. in the oleic acid content, a slight diminution in that of butyric acid, and a more definite temporary fall in the stearic acid figures. The precise character of these seasonal changes in the milk fat of cows is not easy to establish, since other factors also come into play, notably and almost certainly the slight variations in composition in the milk fats of different individuals, and of the same individual as the number of lactations increases.

It is remarkable, however, that exactly the same changes are to be found in the case of the milk fat from cows fed on silage (Table 43B [110a]). Here the winter daily diet of 21 lb. of hay and 50-60 lb. of silage would have been almost identical in its proportions of lipids, carbohydrates and proteins with a diet of approximately 120 lb. of pasture grass daily; yet the same increase in oleic acid content was noticed when the cows went out to grass. The unsaturation of the 1941 summer milk fats (secreted by comparatively young animals) is somewhat lower than that of summer samples previously studied, but this accords with the experience of Dean and Hilditch [97] that the unsaturated components (especially oleic acid) gradually augment with increasing age of the cows. The cause of the fall in oleic acid content during winter is thus not the ingestion of different dietary constituents from those in the summer food, but must lie in some other seasonal change such as temperature or, perhaps more likely, difference in freedom of movement and exercise.

The *diethenoid* C_{18} *acids of cow milk fat* have been the subject of much discussion. Hilditch and Miss Jones [95] mentioned in 1929 that the acids then recorded as linoleic failed to give the usual yields of the tetrahydroxystearic acids (m.p. 155° and 173°) characteristic of linoleic acid from vegetable sources. In 1933, Bosworth and Brown [87] could not detect any linoleic acid in butter fat, whilst Eckstein [99] could only find minute amounts of linoleic and linolenic acids, when isolated in the form of their characteristic tetra- or hexa-bromo-additive products. Green and Hilditch [100] showed that the polyethenoid unsaturation of the C_{18} acids was not due, beyond a very limited extent, to tetra- or even tri-ethenoid unsaturation, and also found that the products of disruptive oxidation were the same (hexanoic and azelaic acids) as from seed fat linoleic acid; like previous workers, they obtained variable, but only small, yields of the tetrahydroxystearic acids, m.p. 155° and 173°, when the C_{18} unsaturated acid fractions were oxidised with alkaline permanganate. The present position has been stated by Brown [101] and by

Hilditch[102] as follows: whilst ordinary or seed fat linoleic acid occurs in only minute proportions in cow milk fat, there is a certain proportion (3–5 per cent. of the total fatty acids) of octadecadienoic acids which appear to be different geometrical (*cis-trans*) isomerides of the $\triangle^{9, 12}$-acid. It has already been mentioned above (pp. 89, 108) that a similar state of affairs holds for the diethenoid C_{18} acids of ox depot and liver glycerides, and liver phosphatides. Hilditch and Jasperson[110a] re-examined the question but obtained little further definite information, except that traces of a triethenoid C_{18} acid were detected, and that, by low-temperature crystallisation, a concentrate of the diethenoid acids (iodine value 134·8) was obtained, the absorption spectrum of which indicated a small proportion of conjugated diethenoid C_{18} acid; this only corresponded, however, to 0·5 per cent. or less of the total butter fatty acids. Later, they[110b] confirmed these findings and also showed that alkali isomerisation at 170–180° led to the formation of much more conjugated diene and slightly more conjugated triene acids, and calculated from the latter data the total proportions of unconjugated octadecadienoic and octadecatrienoic acids (the latter extremely small) in cow and goat milk fats.

In contrast, it may be mentioned that Bosworth[103] was able to obtain without difficulty the characteristic tetrabromostearic acid, m.p. 114°, from the unsaturated acids of human milk fat (*cf.* human milk fat, p. 128).

The *lower saturated acids of milk fats,* although collectively not so prominent as either oleic or palmitic acid, are the constituents which qualitatively differentiate most milk fats from all other fats. In *cow milk fat,* the acids from butyric to lauric account for about 18 to 22 mols. per 100 mols. of the total component acids; of these butyric usually amounts to 8–11 mols. per cent., and hexanoic 3–4 mols. per cent. Butyric acid is thus the most abundant of the lower saturated acids in cow milk fat, but this statement does not apply to the milk fats of some other animals. It will be seen, however, that the milk fat of the buffalo (Tables 45A and 45B, p. 125) is closely similar to that of the domestic cow in its component fatty acids.

The *lower unsaturated acids of cow milk fats* have already been discussed on p. 113. There is, finally, a very small proportion of *highly unsaturated acids of the C_{20-22} series* (or " arachidonic " type) present in cow milk fats as in the corresponding depot fats (*cf.* pp. 89, 97).

The component acids (quoted in Table 43B) of the colostrum fat from an individual cow examined by Baldwin and Longenecker[123b] fall closely within the range of those of milk fats from pasture-fed cows so far as the unsaturated acids, and also most of the saturated acids, are concerned. The palmitic acid content, however, is somewhat higher than the average for cow milk fats, whilst the butyric and hexanoic acid contents are slightly lower; but it is of course not possible to say whether these differences are characteristic for cow colostrum fat, or due to the individual animal studied.

The mode of production of the characteristic milk fats of animals in the mammary glands is a subject which invites discussion. The composition of the milk fats finally produced may, in certain circumstances, provide material of use in suggesting processes which may be operative. This becomes more likely since it has been established independently by Kay *et al.*,[105] by Maynard, McCay *et al.*,[106] and by Shaw and Petersen[111] that the precursors of milk fat are the neutral glycerides present in the blood, and not blood phosphatides or cholesterol esters. Shaw, Powell and Knodt[112] found from the mean of five experiments that the quantity of blood glycerides which disappeared during passage through the mammary gland would account for about 93 per cent. of the milk fat secreted, whilst that of the blood glucose which was similarly removed would account for about 105 per cent. of the lactose found in the milk. To utilise the constitutive information on milk fats fully for such discussion involves, however, the question of their characteristic component glycerides as well as fatty acids, and the matter will therefore be deferred until their glyceride structure has been considered (Chapter VII, pp. 306–310). It may, however, be mentioned here that amongst the points which appear to be important to bear in mind are (i) the relative constancy of the palmitic acid content, (ii) the reciprocal relationship between the proportion of oleic acid on the one hand, and the sum of those of the lower saturated acids and of stearic acid on the other, and (iii) the occurrence of lower mono-ethenoid acids (down to, but not below, C_{10}) in milk fats, in each of which the unsaturated group occupies the same position (Δ^9) relative to the carboxyl group as it does in oleic acid.

Effect of fasting or of certain pathological conditions on the component acids of cow milk fats. It seems to be significant that the effects of fasting and of conditions such as ketosis, whilst not wholly interrupting the secretion of milk fat by the cow, cause the composition of the milk fat to be widely altered from normal. In particular, the proportions of butyric and the other lower saturated acids are much reduced, whilst the oleic acid content is correspondingly increased. In other words, the milk fat from a starving cow, or a cow suffering from severe ketosis, resembles the depot fats in its component acids, rather than a normal milk fat. It is not unreasonable to infer that a normal metabolic conversion of oleo-glycerides into lower saturated " milk fat " glycerides has been disturbed by the abnormal condition of the cow.

The effect of fasting (inanition) on the component acids of cow milk fat was first observed by Smith and Dastur,[91] who recorded the striking detailed analyses given in Table 44A.

It will be noticed that, for instance, in the case of Cow No. 1, the molar contents of the C_4–C_{14} acids fall during fasting by a total of 24·2 per cent., whilst those of the C_{18} acids (oleic, stearic and octadecadienoic) increase by a total of 24·7 per cent. It must be admitted that these figures are extremely suggestive.

Again, Shaw *et al.*,[112, 113] have shown from general characteristics of saponification, Reichert-Meissl, Polenske and iodine values that in severe ketosis the short chain fatty acids of cow milk fat fall considerably below normal, whilst the oleic acid content augments. On treatment by glucose therapy the cow recovers and concurrently the milk fat reverts to its normal composition. These workers have stated that the lower saturated acids of the milk fat are not decreased nearly as much by ketosis as by short periods of fasting, although the blood glucose is usually lowered at least 50 per cent. more by severe ketosis than by a few days of fasting. Qualitatively, however, the alterations produced in cow milk fat both by lack of food and by ketosis are similar, and are consistent with less profound alteration of the blood glycerides than that which takes place during their normal transformation into milk fat.

TABLE 44A. *COMPONENT ACIDS OF COW MILK FAT PRODUCED DURING FASTING (SMITH AND DASTUR* [91]*)*
(MINOR UNSATURATED COMPONENTS INCLUDED)

	Cow No. 1		Cow No. 2
	Before Fasting	During Fasting*	During Fasting†
Acid	(i) *Weight Percentages*		
Butyric	3·5	1·2	2·7
n-Hexanoic (caproic)	0·6	—	0·1
n-Octanoic (caprylic)	1·0	0·1	0·1
n-Decanoic (capric)	1·8	0·2	1·0
Lauric	2·5	0·1	0·6
Myristic	11·9	2·8	3·8
Palmitic	23·5	20·0	22·1
Stearic	11·6	14·3	9·9
Arachidic	1·1	0·9	0·9
Δ^9-Decenoic	0·2	—	0·2 ‡
Δ^9-Dodecenoic	0·2	—	0·2 ‡
Δ^9-Tetradecenoic	0·9	0·4 ‡	0·4 ‡
Δ^9-Hexadecenoic	3·2	1·4	2·0
Oleic	35·9	52·8	51·7
Octadecadienoic	1·2	2·5	0·8
C_{20} unsaturated	0·8	3·3	3·5
	(ii) *Molar Percentages*		
Butyric	9·7	3·5	7·9
n-Hexanoic	1·2	—	0·1
n-Octanoic	1·6	0·2	0·2
n-Decanoic	2·5	0·3	1·5
Lauric	3·0	0·2	0·7
Myristic	12·5	3·2	4·3
Palmitic	22·1	20·9	22·1
Stearic	9·8	13·5	8·9
Arachidic	0·8	0·8	0·8
Δ^9-Decenoic	0·3	—	0·2
Δ^9-Dodecenoic	0·3	—	0·3
Δ^9-Tetradecenoic	1·0	0·5	0·5
Δ^9-Hexadecenoic	3·0	1·5	2·0
Oleic	30·5	50·1	46·9
Octadecadienoic	1·0	2·4	0·7
C_{20} unsaturated	0·6	2·9	2·9

* Sample from mixed fat secreted on 11th and 12th days of inanition.
† Pooled sample from fat secreted on the last six days (7th–12th) of inanition.
‡ Figures marked thus are probably somewhat higher than the true values (owing to difficulty of determining the small proportions in question).

Component acids of milk fats from cows receiving specific fatty oils in their diets. Two groups of investigations may be considered separately in this connection :

(i) A few studies have been made by Hilditch and Sleightholme [96] and by Hilditch and Thompson [98] of the fats from the milk of Berkshire cows which had been given a regular ration of one or other fatty oil for some time previous to the period at which the milk was taken.

(ii) In another investigation Hilditch and Jasperson [114] examined the milk fats of Ayrshire heifers from a Cheshire farm in which a basal control diet was supplemented with 8 ounces daily of refined groundnut oil, groundnut oil hydrogenated to iodine values of 45 or 17, or refined palm kernel oil (iodine value 17). This series was undertaken in view of a report by Brown, Dustman and Weakley [115] that almost completely hydrogenated soya bean oil fed to cows caused a slight increase in the iodine value of the milk fat, which these authors ascribed to desaturation of the stearic glycerides in the hydrogenated fat.

The results of all these studies are summarised in Tables 44B and 44C.

TABLE 44B. *COMPONENT ACIDS OF COW MILK FATS (EFFECT OF ADDED FATS IN DIETS)*

Fat added to basal ration :

Coconut oil cake	7 lb. coconut cake daily for two weeks previously.
Soya bean cake	5·2 lb. soya bean cake daily for two weeks previously.
Linseed oil	4 ounces linseed oil daily for two weeks previously.
Rape oil	4 ounces rape oil daily for two weeks previously.
Cod liver oil	4 ounces cod liver oil daily for two weeks previously.

(*a*) Minor unsaturated components not included.
(*b*) Minor unsaturated components included.

INGESTED FAT:	COCONUT CAKE [96] (*a*)	SOYA BEAN CAKE [96] (*a*)	LINSEED OIL [98] (*a*)	RAPE OIL [98] (*b*)	COD LIVER OIL [98] I (*a*)	COD LIVER OIL [98] II (*b*)
ACID			(i) *Weight Percentages*			
Butyric	3·4	3·6	4·2	3·6	2·1	2·0
n-Hexanoic	2·0	1·5	2·0	1·6	0·9	0·6
n-Octanoic	1·1	1·7	1·3	1·0	0·5	0·6
n-Decanoic	3·2	3·8	2·3	1·5	1·2	1·3
Lauric	7·3	6·5	3·1	1·8	3·1	0·9
Myristic	17·1	10·6	8·4	8·1	6·4	8·4
Palmitic	27·0	26·3	21·8	20·3	22·7	25·4
Stearic	4·8	8·3	9·9	13·8	6·7	8·2
as Arachidic	—	1·2	0·6	0·5	0·6	0·6
as Decenoic	—	—	—	0·2	—	0·5
as Tetradecenoic	—	—	—	1·3	—	1·4
as Hexadecenoic	—	—	—	2·4	—	3·3
Oleic	31·7	32·9	39·3	36·0	43·3	37·8
as Octadecadienoic	2·4	3·6	5·9	3·3	4·8	3·9
as C_{20-22} unsaturated	—	—	1·2	1·0	7·7	5·1
as Erucic	—	—	—	3·6	—	—
			(ii) *Molar Percentages*			
Butyric	9·0	9·6	11·2	9·9	6·1	5·7
n-Hexanoic	3·9	3·0	4·1	3·4	2·0	1·2
n-Octanoic	1·7	2·8	2·1	1·6	0·8	1·0
n-Decanoic	4·3	5·1	3·1	2·2	1·8	1·9
Lauric	8·3	7·5	3·6	2·2	3·9	1·1
Myristic	17·2	10·7	8·6	8·6	7·1	9·3
Palmitic	24·1	23·7	20·0	19·1	22·4	25·1
Stearic	3·9	6·7	8·2	11·7	6·0	7·3
as Arachidic	—	0·9	0·4	0·4	0·5	0·5
as Decenoic	—	—	—	0·2	—	0·8
as Tetradecenoic	—	—	—	1·4	—	1·5
as Hexadecenoic	—	—	—	2·3	—	3·3
Oleic	25·7	27·0	32·8	30·8	38·8	33·8
as Octadecadienoic	1·9	3·0	5·0	2·9	4·4	3·5
as C_{20-22} unsaturated	—	—	0·9	0·7	6·2	4·0
as Erucic	—	—	—	2·6	—	—

The effects of the ingested vegetable fats on the milk fats in Table 44B were comparatively slight, but certain points of interest appeared. Comparison should, of course, be made with the cow milk fats from animals on normal stall-fed or pasture diets already given in Tables 43A and 43B.

Coconut oil, which is rich in lauric and myristic acids (*cf.* Chapter IV, Table 59B, p. 200), has apparently little effect on most of the component

TABLE 44c. *COMPONENT ACIDS OF COW MILK FATS (EFFECT OF ADDED FATS IN DIETS)*

(Minor unsaturated components included)

INGESTED FAT:	CONTROL	PALM KERNEL OIL	GROUNDNUT OIL	HYDROGENATED GROUNDNUT OIL	
ACID	(Hay, swedes, oats)	(I.V.17)	(I.V.88)	(I.V.45)	(I.V.17)
		(i) *Weight Percentages*			
Butyric	4·0	3·2	2·9	2·7	3·6
n-Hexanoic	2·3	1·7	1·5	1·5	2·1
n-Octanoic	0·8	1·2	0·5	0·6	1·2
n-Decanoic	1·9	1·3	1·4	1·5	1·5
Lauric	2·2	6·0	1·7	2·0	1·9
Myristic	9·3	10·9	7·3	6·2	8·2
Palmitic	25·5	22·2	23·8	21·8	24·9
Stearic	11·8	12·0	12·7	16·6	13·8
as Arachidic	0·8	1·1	1·2	1·0	1·2
Decenoic	0·2	0·1	0·1	0·1	0·1
Dodecenoic	0·2	0·4	0·2	0·2	0·2
Tetradecenoic	0·9	1·0	0·7	0·6	0·8
Hexadecenoic	2·3	2·3	2·1	2·3	1·5
Oleic	34·3	33·5	40·6	39·0	35·6
Octadecadienoic	2·1	1·2	1·8	3·3	1·7
C_{20-22} unsaturated	1·4	1·9	1·5	0·6	1·7
		(ii) *Molar Percentages*			
Butyric	10·5	8·6	8·2	7·6	9·8
n-Hexanoic	4·6	3·4	3·2	3·3	4·3
n-Octanoic	1·3	1·9	0·8	0·9	1·9
n-Decanoic	2·7	1·8	1·9	2·1	2·1
Lauric	2·6	7·1	2·1	2·4	2·3
Myristic	9·6	11·3	7·9	6·7	8·5
Palmitic	23·4	20·6	22·8	21·0	23·2
Stearic	9·7	10·0	10·9	14·4	11·6
as Arachidic	0·6	0·8	1·0	0·8	0·9
Decenoic	0·3	0·2	0·1	0·1	0·2
Dodecenoic	0·2	0·5	0·2	0·2	0·2
Tetradecenoic	1·0	1·1	0·8	0·6	0·8
Hexadecenoic	2·1	2·2	2·1	2·2	1·4
Oleic	28·6	28·1	35·2	34·4	30·0
Octadecadienoic	1·8	1·0	1·6	2·9	1·5
C_{20-22} unsaturated	1·0	1·4	1·2	0·4	1·3

acids, but the lauric and myristic acids are each present in about twice the usual amount. This suggests that some of the lauromyristins, present in quantity in coconut fat, may have passed directly into the milk fat. A similar result is seen in Table 44c in the case of *palm kernel oil*; the lauric and myristic acid contents are definitely increased (especially the former), indicating transference of some of the dilauromyristins which predominate in palm kernel oil into the milk fat, with a consequent slight reduction in the oleic and palmitic acid contents of the milk fat.

The results of ingestion of *soya bean cake* and *linseed oil* are interesting chiefly because, in spite of the high linoleic content of both oils and of high linolenic acid content in linseed oil, the amount of polyethenoid C_{18} acids in the milk fats showed no significant increase. Moreover, the latter acids yielded no insoluble tetra- or hexa-bromostearic acids, and only very small amounts of the tetrahydroxystearic acid, m.p. 155°. The results thus strongly suggest that neither the linoleic nor the linolenic acid of seed fats are readily assimilated by cows or, at least, that they are not retained as such by the mammary gland of this animal. For the rest, these two milk fats showed no great divergence from normal, other than perhaps a fairly high oleic acid figure in the fat from the cow which had received linseed oil. It may be of minor significance that the apparent arachidic acid figure is higher than usual in the fat from the cow which received soya bean cake, since this acid is present in soya bean oil as a minor component (for the component acids of soya bean and linseed oils, see respectively Chapter IV, Table 57, p. 189, and Table 49, p. 157).

Rape oil, similarly, has little effect on the milk fat component acids unless to increase the oleic acid slightly, at the general expense of the remaining constituents, especially, perhaps, palmitic acid. In this case there was definite evidence of the infiltration of a small proportion of erucic acid (which forms 45–50 per cent. of the acids of rape oil, *cf.* Chapter IV, Table 56, p. 184); but seed fat linoleic acid, which is also present in rape oil to the extent of 25–30 per cent., was, as usual, not detected with certainty.

The results of feeding *cod liver oil* to cows stand quite apart from the rest of the data included in Table 44B. The outstanding features are: (i) the great reduction (of the order of 50 per cent.) in the amount of lower saturated acids; (ii) a proportionately similar increase in oleic acid; (iii) no great difference from the normal in the amount of octadecadienoic acid; (iv) the presence of about 5 per cent. of C_{20-22} unsaturated acids instead of the 1 per cent. (or thereabouts) of these acids normally present; and (v) the absence of any increase in the small amount of hexadecenoic acid, although this acid is almost as prominent a component of the cod liver oil acids as the C_{20-22} acids. These effects, which are accompanied by a reduction of the fat content of the milk, are probably significant not only from the practical standpoint but also from their possible bearing on the metabolism of milk fat. They are even more striking when depicted in the form of the amount of each fatty acid produced daily by the lactating cow than when given as percentages (*cf.* Chapter VII, Table 82, p. 308). This aspect of the results in question, and their possible implications as regards milk fat metabolism, will be returned to later (Chapter VII, p. 306). At this point we will only add that Golding [108] has indicated that the specific effect of cod liver oil on the lactation of the cows is not shown when the unsaponifiable fraction of the oil, instead of the whole oil, is given in the diet, thus pointing to the injurious or active component occurring in part of the triglycerides; that McCay and Maynard [109] reached the same conclusion in regard to the production of muscular lesions in animals after ingestion of cod liver oil; and that the data in Table 44B show clearly that, in contrast to the absence of infiltration of seed fat linoleic or linolenic acids from the diet, the highly unsaturated C_{20} and C_{22} acids of cod liver oil pass into the milk fat to quite an appreciable extent.

The data in Table 44C resulting from ingestion of 8 ounces daily of *groundnut oil* or *hydrogenated groundnut oils* also merit brief discussion. Although *groundnut oil* contains about 20 per cent. of linoleic acid, the content of octadecadienoic acid in the cow milk fat concerned is not appreciably altered; nor have the arachidic, behenic or lignoceric acids (about 6 per cent. of the groundnut oil, *cf.* Chap. IV, Table 57, and p. 188) passed into the milk fat. About 20 to 30 per cent. of the groundnut oil glycerides, however, contain no linoleic or arachidic and higher acids but are palmitodiolein, stearodiolein or triolein. The main effect of ingested groundnut oil, which consists of significant increase in the milk fat of oleic acid, a slight fall in palmitic, and a large fall in butyric-decanoic acids, may be due to admixture of some or all of these three oleo-glycerides with the normal milk fat, or to slight interference with the normal metabolic processes, whereby the production of the lower saturated glycerides normal to milk fat is restricted.

The hydrogenated groundnut oil of iodine value 45 contained about 52 per cent. of oleic (and *iso*-oleic) acids and about 33 per cent. of stearic acid ; its glycerides were mainly monosaturated dioleins (or *iso*-oleins) (65 per cent.) and mono-oleo- (or *iso*-oleo-) disaturated glycerides (25 per cent.). The effect on the milk fat of feeding this oil was broadly similar to that of groundnut oil itself—increase in oleic acid content, further diminution in palmitic acid, and diminution in butyric-decanoic acids. The increase in stearic acid suggests some passage of oleo-stearo-glycerides from the hydrogenated groundnut oil into the milk.

On the other hand, the milk fat from cows fed on the *hydrogenated groundnut oil of iodine value* 17 is remarkably similar in composition to the control fat, except for a slight increase in oleic acid and a definite increase in stearic acid. About half of this hydrogenated fat consists of fully saturated glycerides (tristearin, etc.) of high melting point, which are only present in the liquid phase in the cow's digestive tract in so far as they may be held in solution by the remaining part of the fat, which consists of mono-oleo-disaturated glycerides such as oleodistearin. It has indeed been established [116] many years ago that tristearin or, indeed, any fat melting much above 50° is largely excreted unchanged when fed to animals. The only portions of this hydrogenated groundnut oil to pass into the blood stream would therefore be mono-oleo-disaturated glycerides (in which oleodistearin would predominate), and this is reflected in the slightly increased proportions of the corresponding component acids in the resulting milk fat.

The detailed analyses show, in fact, that the observed effects are wholly accounted for by taking into consideration the non-assimilation of the high-melting fully saturated glycerides, the relatively small or negligible conversion of linoleo-glycerides and certain other acyl glycerides into cow milk fat, and the absorption of a certain proportion of oleodistearin into the milk fat. It is quite unnecessary to presume that desaturation of stearo-glycerides takes place in the case of ingested highly hydrogenated fats, as supposed by Brown, Dustman and Weakley [115] ; indeed, the analytical figures show increases in both stearic and oleic acid contents as compared with the control milk fat.

Component acids of cow milk phosphatides. Until it was demonstrated in 1936 [105] and confirmed later [106, 111] that blood phosphatides are unaltered during passage of blood through the mammary gland of the cow, but that blood glycerides disappear as milk fat is produced, it was widely supposed that phosphatides played an important part in the production of the characteristic glycerides of cow milk. It is thus somewhat curious that the component acids of cow milk phosphatides were not studied in any detail until 1934. In that year Kurtz, Jamieson and Holm [107] examined the phosphatides from buttermilk powder and found that part was insoluble in ether at 0° : the acids in this fraction contained about 80 per cent. of lignoceric acid, the rest being a complex mixture of saturated, unsaturated, and hydroxy-acids, and this material was probably a mixture of sphingomyelin and cerebrosides. The acids of the ether-soluble portion were more akin to the usual fatty acids, and their composition as determined by Kurtz *et al.*[107] is given below.

In 1941 Hilditch and Maddison[117] examined two specimens of crude phosphatides separated respectively from Swiss butter fat and from English butter fat clarification residues. The results of component acid analyses on these materials are also given below. It will be noticed that they contained a certain amount of higher saturated acids (calculated arbitrarily as $C_{26}H_{52}O_2$) from wax or cerebroside compounds admixed with the crude phosphatides.

COMPONENT ACIDS (WTS. PER CENT.) OF COW MILK PHOSPHATIDES

	Kurtz *et al.*[107]	Hilditch and Maddison[117]	
ACID		SWISS	ENGLISH
Myristic	5·2	3·2	5·5
Palmitic	—	21·0	13·4
Stearic	16·1	7·3	9·0
as Arachidic	1·8	12·3	20·9
as $C_{26}H_{52}O_2$	—	5·2	10·0
Hexadecenoic	—	4·3	4·9
Oleic	70·6	32·5	23·5
Octadecadienoic	—	6·4	—
C_{20-22} unsaturated	6·3	7·8	12·8

Clearly, the phosphatide component acids differ entirely from those of cow milk glycerides. Acids of lower molecular weight than myristic are completely absent, so that the lower saturated acids—the most characteristic of the cow milk fat acids—have no counterpart in the cow milk phosphatide acids. These, however, resemble those of cow liver and other animal liver phosphatides (*cf.* Table 41, p. 109) in their general composition, and especially in the presence, entirely characteristic for phosphatides, of notable proportions of highly unsaturated acids of the C_{20} and C_{22} series which furnish the polybromo-additive compounds which darken and partially melt at 210–220°. In detail the three sets of data are not accordant; the presence of higher saturated acids (from non-phosphatidic compounds) complicates the analyses of Swiss and English butter phosphatides, and the absence of palmitic acid and the very high oleic content present unusual features in the analysis by Kurtz *et al.* In all three cow milk phosphatides, nevertheless, the general resemblance to other animal phosphatides is as marked as is their essential difference in fatty acid composition from the cow milk glycerides.

Component acids of milk fats of other herbivorous mammals. The milk fats of a moderate number of species of animals, other than the cow, have been examined in detail. Table 45A gives data for goat, sheep, camel and buffalo milk fatty acids (calculated without allowance for minor unsaturated acids), Table 45B similar data (including minor unsaturated components) for buffalo milk fatty acids, and Table 45C similar data (including minor unsaturated components) for other goat and sheep milk fats, and for those of the sow and mare.

Comparing the molar percentages of the acids in Tables 45A, 45B and 45C, it is clear that (with the exception of mare milk fat) the proportion of palmitic acid does not vary greatly in the milk fats of any of the species listed. The buffalo, sow and camel approach the value of 30 per cent. (mol.) which is characteristic for the depot fats of oxen, pigs and many other animals.

TABLE 45A. *COMPONENT ACIDS OF GOAT, SHEEP, CAMEL, AND BUFFALO MILK FATS*
(*MINOR UNSATURATED COMPONENTS NOT INCLUDED*)

ACID	GOAT [92] INDIAN	SHEEP [92] INDIAN	CAMEL [93] INDIAN	BUFFALO [94] INDIAN	BUFFALO [118] TURKISH
	(i) *Weight Percentages*				
Butyric	3·0	3·3	2·1	4·1	4·3
n-Hexanoic (caproic)	2·3	2·8	0·9	1·4	1·3
n-Octanoic (caprylic)	3·9	3·8	0·6	0·9	0·4
n-Decanoic (capric)	8·6	7·8	1·4	1·7	Trace
Lauric	4·6	5·4	4·6	2·8	3·0
Myristic	11·5	12·2	7·3	10·1	7·3
Palmitic	24·7	23·5	29·3	31·1	26·1
Stearic	9·3	6·9	11·1	11·2	16·5
as Arachidic	0·1	1·9	—	0·9	3·3
Oleic	30·5	28·3	38·8	33·2	35·8
as Octadecadienoic	1·5	4·1	3·8	2·6	2·0
	(ii) *Molar Percentages*				
Butyric	7·6	8·4	5·9	10·9	11·8
n-Hexanoic	4·5	5·4	1·9	2·8	2·7
n-Octanoic	6·2	5·8	1·1	1·5	0·7
n-Decanoic	11·1	10·1	2·1	2·4	Trace
Lauric	5·1	6·0	5·7	3·3	3·7
Myristic	11·2	11·8	7·9	10·5	7·8
Palmitic	21·5	20·4	28·3	28·7	24·5
Stearic	7·3	5·4	9·7	9·3	14·0
as Arachidic	0·1	1·3	—	0·7	2·5
Oleic	24·2	22·2	34·1	27·7	30·6
as Octadecadienoic	1·2	3·2	3·3	2·2	1·7

TABLE 45B. *COMPONENT ACIDS OF INDIAN BUFFALO MILK FATS* [124]
(*MINOR UNSATURATED COMPONENTS INCLUDED*)

Reichert-Meissl value of fat	37·4	30·8	22·7	20·7
Iodine value of fat	27·4	28·9	34·9	37·0
ACID	(i) *Weight Percentages*			
Butyric	5·8	5·0	3·7	4·1
n-Hexanoic	0·6	0·2	0·3	—
n-Octanoic	0·9	0·3	1·3	0·1
n-Decanoic	1·0	0·6	1·3	0·3
Lauric	1·6	2·0	2·1	0·6
Myristic	9·0	11·9	6·7	4·4
Palmitic	35·2	34·2	23·7	25·8
Stearic	15·3	12·2	19·7	21·7
as Arachidic	0·1	—	1·3	1·4
Decenoic	0·1	0·1	0·2	Trace
Dodecenoic	0·1	0·1	0·2	0·1
Tetradecenoic	0·6	1·0	0·8	0·5
Hexadecenoic	3·3	3·2	5·3	3·0
Oleic	20·5	27·6	33·2	36·2
Octadecadienoic	1·5	0·5	0·2	1·1
C_{20-22} unsaturated	4·4	1·1	—	0·7
	(ii) *Molar Percentages*			
Butyric	15·4	13·5	10·1	11·5
n-Hexanoic	1·1	0·4	0·7	—
n-Octanoic	1·4	0·5	2·2	0·1
n-Decanoic	1·4	0·9	1·8	0·5
Lauric	1·9	2·4	2·6	0·8
Myristic	9·2	12·3	7·1	4·8
Palmitic	31·9	31·5	22·5	25·1
Stearic	12·5	10·1	16·8	19·0
as Arachidic	0·1	—	1·0	1·1
Decenoic	0·1	0·1	0·3	Trace
Dodecenoic	0·1	0·1	0·2	0·1
Tetradecenoic	0·6	1·0	0·8	0·5
Hexadecenoic	3·0	3·0	5·1	2·9
Oleic	16·8	23·0	28·6	32·0
Octadecadienoic	1·2	0·4	0·2	1·0
C_{20-22} unsaturated	3·3	0·8	—	0·6

TABLE 45c. *COMPONENT ACIDS OF GOAT, SHEEP, SOW AND MARE MILK FATS*

ACID	GOAT [88] U.S.A.	GOAT [120] ENGLISH	SHEEP [120] ENGLISH	SOW [119] NEW ZEALAND	MARE [120] ENGLISH
		(i) *Weight*	*Percentages*		
Butyric	2·1	3·0	2·8	1·3	0·4
n-Hexanoic	1·9	2·5	2·6		0·9
n-Octanoic	2·7	2·8	2·2		2·6
n-Decanoic	7·9	10·0	4·8		5·5
Lauric	3·5	6·0	3·9		5·6
Myristic	10·2	12·3	9·7	1·5	7·0
Palmitic	28·7	27·9	23·9	26·9	16·1
Stearic	8·1	6·0	12·6	6·5	2·9
as Arachidic	0·4	0·6	1·1	—	0·3
Decenoic	0·2	0·3	0·1	—	0·9
Dodecenoic	—	0·3	0·1	—	1·0
Tetradecenoic	0·4	0·8	0·6	—	1·8
Hexadecenoic	2·1	2·6	2·2	8·3	7·5
Oleic	31·1	21·1	26·3	36·7	42·4 (−3·7H)
Octadecadienoic	—	3·6	5·2	14·6	
C_{20-22} unsaturated	0·7	0·2	1·9	4·2	5·1
		(ii) *Molar*	*Percentages*		
Butyric	5·6	7·5	7·5	2·4	1·1
n-Hexanoic	3·8	4·7	5·3		1·9
n-Octanoic	4·3	4·3	3·5		4·4
n-Decanoic	10·6	12·8	6·4		7·9
Lauric	4·0	6·6	4·5		6·8
Myristic	10·3	11·8	9·9	1·8	7·4
Palmitic	25·9	24·1	21·6	28·3	15·4
Stearic	6·6	4·7	10·3	6·1	2·4
as Arachidic	0·3	0·4	0·8	—	0·2
Decenoic	0·3	0·3	0·2	—	1·3
Dodecenoic	—	0·3	0·2	—	1·2
Tetradecenoic	0·4	0·8	0·6	—	1·9
Hexadecenoic	1·9	2·2	2·0	8·8	7·2
Oleic	25·5	16·5	21·6	35·0	36·9
Octadecadienoic	—	2·8	4·3	14·0	
C_{20-22} unsaturated	0·5	0·2	1·3	3·6	4·0

This figure is appreciably lower in sheep and goat milk fats (20–26 per cent. mol.), and it may be recalled that the palmitic acid content of sheep depot fats (Tables 31, 32) is usually about 4 or 5 per cent. lower than that of ox depot fats.

The oleic acid content, as usual, varies somewhat widely, even in the case of milk fats of the same species of animal. Thus in the three goat milk fats the range of oleic acid content is 16·5–25·5 per cent. (mol.) and, curiously, the English goat milk contains the lowest proportion—nearly 10 units per cent. lower than that from the Indian goat, which presumably enjoyed a warmer climate.

The most striking differences, however, are manifested in the contents and kinds of the lower saturated acids present. In buffalo milk the proportion of butyric and of the other lower acids up to lauric are indistinguishable from those of cow milk fats, but in no other species (in the group available for discussion) do the proportions of butyric acid in the milk fats reach those of the bovine group. The detailed component acid analyses of buffalo milk fats (ghee) of differing Reichert-Meissel and iodine values given by Achaya and Banerjee[124] (Table 45B), again reveal general constancy of the palmitic acid content and an inverse relationship between the proportion of oleic acid on the one hand and, on the other, of (*a*) the lower (C_4–C_{14}) saturated acids and (*b*) stearic acid. The milk fats with very high (17 and 19 per cent. mol.) stearic acid resulted after intensive feeding of the buffalo cows with cotton-seed.

In the milk fats of sheep and goats the butyric acid content is already reduced by about one quarter (compared with bovine milk fats), although the total content of butyric-decanoic acids amounts to 25–30 per cent. (mol.) of the total fatty acids—even higher than in cow and related milk fats. This is in consequence of specifically high proportions of decanoic (capric) and, to a less degree, octanoic (caprylic) acids in goat and sheep milk fats; the molar percentage of decanoic acid frequently reaches 10 or even somewhat higher in goat milk fats.

Camel milk fat appears to contain about half the proportion of butyric acid present in bovine milk fats, and somewhat more than this proportion of the C_6, C_8 and C_{10} acids, the amount of oleic acid being correspondingly increased; whilst in sow and mare milk fats it would appear that the lower saturated acids occur only in very minor quantities, or even traces, so that to a large extent these milk fats tend to resemble the corresponding depot fats in the qualitative, and also perhaps the quantitative, aspects of their component acids.

In addition to the data given by de la Mare and Shorland [119] for *sow milk fat* (a semi-micro analysis carried out on about 9 grams of fat from 130 c.c. of sow milk), the component acids were given earlier by Laxa,[104] apparently from the Reichert-Meissl (2·1), Polenske (1·2), iodine (58·2) and saponification (193·9) values, as caprylic and capric 1·5, myristic 2·7, palmitic 28·0, and oleic 67·8 per cent. These figures, from their nature only a rough approximation, give general confirmation to the more precise data of de la Mare and Shorland. The latter authors note the high content (14·6 per cent. wt.) of octadecadienoic acid in sow milk fat, and report that this failed to give more than traces of petrol-insoluble tetrabromo-adducts; they suggest that the high proportion of this acid might be due to pasture lipids which may contain an isomeric form of linoleic acid.

This, however, is not consistent with the much smaller contents of octadecadienoic acids in the milk fats of sheep, goats and cows, in all of which, again, it has been observed that these acids do not include more than traces of the ordinary or seed fat linoleic acid. The absence of the latter from the diethenoid C_{18} acids in the milk fats of the cow, ewe, goat and sow, and in the depot fats of oxen and sheep, is one of the most characteristic features of all these fats. On the other hand it is curious that the octadecadienoic acids of pig depot fats (usually present to the extent of only 5 to 7 per cent.) contain a fair proportion of the ordinary linoleic acid which yields the petrol-insoluble crystalline tetrabromostearic acid, m.p. 114° (*cf.* p. 97).

The milk fat of the *mare* [120] has several points of difference from others in Table 45C. Its content of butyric acid, whilst definite, is only about one-tenth of that in cow milk fats; decanoic, lauric and myristic acids each contribute about 7 per cent. (mol.). The palmitic acid content (15·4 per cent) appears unusually low for a milk fat, but hexadecenoic acid (7·2 per cent.) is higher than usual, so that the total C_{16} acid content approaches 23 per cent. (mol.) of the total fatty acids. The unsaturated C_{20} and C_{22} acids are somewhat more prominent than in most milk fats, but the outstanding feature is the constitution of the unsaturated C_{18} acids. Here linolenic acid (the " seed-fat " form which gives a hexabromostearic acid, m.p. 181°) forms about 14 per cent. of the total fatty acids, the rest of the unsaturated C_{18} acids being oleic (16 per cent.) and octadecadienoic (7 per cent.), the latter being probably the " seed-fat " or linoleic form. The low proportion of oleic acid and the presence of substantial amounts of " seed-fat " linolenic combine to place the mare milk fat apart from any other milk fat yet examined.

Component acids of human milk fat. It has long been known that human milk fat has marked differences in analytical characteristics from cow milk fat. Thus in 1928 Elsdon [121] recorded Reichert-Meissl 3·4, Polenske 1·9, Kirscher 2·0, iodine value 35·9, for a mixed sample of human milk fat at an early stage of lactation, giving the percentages of lactose, protein and fat in human milk as 6·8–6·9, 2·1–1·3, and 2·9–3·6, respectively, as the stage of lactation increased (1–7 days, 8–28 days, and 1–9 months).

In 1934 Bosworth [103] separated the acids from about 3 lbs. of human milk fat (saponification equivalent 273·4, iodine value 56·2, Reichert-Meissl value 2·5, Polenske value 0·1) into thirty fractions by distillation of the methyl esters. He found that the amount of butyric and hexanoic acids, if any, was extremely small, and that at least 0·02 per cent. of decenoic and 0·6 per cent. of tetradecenoic acids were present, but did not deduce the proportions of any other acids from his ester-fractionation data ; independent calculations, however, show that his data lead to a fatty acid composition closely in agreement with the figures given below in Table 46. Bosworth made the important observation that the octadecadienoic acids of human milk fat include considerable proportions of the ordinary or " seed fat " linoleic acid (*cis-cis*-$\Delta^{9,12}$-octadecadienoic acid), as shown by isolation of the characteristic petrol-insoluble tetrabromostearic acid, m.p. 113°.

In 1944 Hilditch and Meara [122] determined the component acids of four human milk fats (from early, full, and late lactation periods) with the results given in Table 46A, and Baldwin and Longenecker [123a] determined those of human colostrum and milk fats (Table 46B).

The saturated acids of human milk fats in Tables 46A and 46B present notable differences from those of cow (and other) milk fats. Although palmitic acid (the main saturated acid at about 22–24 per cent), stearic and myristic acids are present in proportions similar to those in which they occur in cow milk fats, the lower members of the series are quite different, and include only lauric and small proportions of decanoic acid. Careful examination of the steam-volatile acids from each specimen of milk fat studied by Hilditch and Meara [122] failed to reveal the presence of any butyric acid or of other acids of lower molecular weight than decanoic acid. Hence, whereas in cow milk fat, out of every 100 mols. of fatty acids, about 10 mols. consist of butyric acid, 4–5 mols. of hexanoic-octanoic acids, and 4–5 mols. of decanoic-lauric acids, in human milk fat the three lower acids are not present and the combined amount of lauric and decanoic acids reaches 10–11 per cent. (mol.), with lauric acid predominating. Baldwin and Longenecker [123a] reported the presence of slightly more than 1 per cent. (mol.) of the three lower acids (chiefly butyric).

Subject to some variation from one specimen to another in mean un-

TABLE 46A. *COMPONENT ACIDS OF HUMAN MILK FATS*[122]

STAGE OF LACTATION:	EARLY	EARLY	FULL	LATE
Iodine value of fat	56·0	52·1	54·7	48·2
ACID	(i) *Weight Percentages*			
Decanoic	2·7	0·8	1·7	0·5
Lauric	5·1	6·1	6·4	7·0
Myristic	8·1	10·8	7·6	13·9
Palmitic	22·5	24·6	22·4	24·1
Stearic	8·3	7·3	9·0	9·6
as Arachidic	1·0	1·8	0·9	—
as Decenoic	Trace	Trace	Trace	Trace
as Dodecenoic	0·1	0·1	0·1	0·1
as Tetradecenoic	1·3	0·4	0·5	0·9
as Hexadecenoic	3·1	3·3	3·7	2·8
Oleic	36·4	32·8	36·6	30·2
Octadecadienoic	7·9	6·3	8·2	5·5
C_{20-22} unsaturated	3·5	5·7	2·9	5·4
	(ii) *Molar Percentages*			
Decanoic	4·2	1·2	2·5	0·8
Lauric	6·7	8·0	8·3	9·0
Myristic	9·2	12·4	8·7	15·8
Palmitic	22·9	25·2	22·8	24·4
Stearic	7·7	6·7	8·3	8·8
as Arachidic	0·8	1·5	0·8	—
as Decenoic	Trace	Trace	Trace	Trace
as Dodecenoic	0·1	0·1	0·2	0·1
as Tetradecenoic	1·5	0·5	0·6	1·1
as Hexadecenoic	3·1	3·4	3·8	2·9
Oleic	33·6	30·4	33·9	27·6
Octadecadienoic	7·3	5·9	7·7	5·1
C_{20-22} unsaturated	2·9	4·7	2·4	4·4

saturation (i.e. mainly in oleic acid content), it would appear that human milk fat component acids consist of saturated and unsaturated fatty acids in not far from equal proportions. In the unsaturated group oleic acid (the chief component acid of the whole fat) amounts to 30–37 per cent. (wt.), the minor components hexa- and tetra-decenoic acids occur in about the same proportions as in cow milk fat and in many animal body fats, but decenoic and dodecenoic acids are probably present in even lower proportions than in cow milk fat. The most arresting features of the unsaturated acids are the proportions of diethenoid C_{18} acids, unusually high for an animal fat and consisting, according to Bosworth[103] and Hilditch and Meara,[112] to a large extent of the linoleic acid characteristic of vegetable seed fats; and the amounts, also relatively high for a land animal fat, of unsaturated acids of the C_{20} and C_{22} series. At least 60 per cent. of the diethenoid C_{18} acids are the form of linoleic (*cis-cis*-$\Delta^{9,12}$-octadecadienoic) acid which is present in seed fats; so that human milk fat apparently differs both in the quantity and the nature of its octadecadienoic acids from all the other animal milk fats which were discussed in the preceding sections—a somewhat surprising circumstance. On the other hand, Baldwin and Longenecker[123a] failed to isolate any crystalline tetrabromostearic acid from their octadecadienoic ester concentrates, and consider that ordinary linoleic acid may therefore only be present in small amounts in human, as in other, milk fats; the values recorded in Table 46B for di-, tri-, and tetra-ethenoid acids observed by these workers are based on spectrophotometric analyses of alkali-

TABLE 46B. *COMPONENT ACIDS OF HUMAN MILK FATS*[128a]

	COLOSTRUM		MILK (MATURE)
	1st–2nd day	3rd day	22nd–43rd day
	(i) *Weight Percentages*		
Butyric	0·2	0·3	0·4
Hexanoic	0·1	0·1	0·1
Octanoic	0·8	0·1	0·3
Decanoic	3·5	0·9	2·2
Lauric	0·9	2·6	5·5
Myristic	2·8	4·9	8·5
Palmitic	24·6	27·8	23·2
Stearic	9·9	7·7	6·9
as Arachidic	4·9	2·7	1·1
Decenoic	0·2	0·1	0·1
Dodecenoic	0·1	0·1	0·1
Tetradecenoic	0·1	0·2	0·6
Hexadecenoic	1·8	2·9	3·0
Oleic	36·0	37·1	36·5
Octadecadienoic	7·5	6·2	7·8
Octadecatrienoic	0·3	0·3	0·4
Eicosadienoic	4·6	4·7	2·4
Eicosatetraenoic	1·8	1·6	0·9
	(ii) *Molar Percentages*		
Butyric	0·7	0·8	1·1
Hexanoic	0·3	0·2	0·1
Octanoic	1·5	0·1	0·6
Decanoic	5·3	1·4	3·3
Lauric	1·2	3·4	7·1
Myristic	3·3	5·7	9·6
Palmitic	25·4	28·9	23·4
Stearic	9·2	7·2	6·3
as Arachidic	4·1	2·3	0·9
Decenoic	0·3	0·1	0·1
Dodecenoic	0·1	0·1	0·1
Tetradecenoic	0·1	0·2	0·7
Hexadecenoic	1·9	3·0	3·0
Oleic	33·8	35·1	33·3
Octadecadienoic	7·1	5·9	7·2
Octadecatrienoic	0·3	0·2	0·4
Eicosadienoic	3·9	4·0	2·0
Eicosatetraenoic	1·5	1·4	0·8

isomerised ester fractions by the method referred to in Chapter IV (" S," p. 138).

The general picture suggested by the data in Tables 46A and 46B is that, whatever is the mechanism of formation of the lower fatty acids in milk fats, this process is carried on much more extensively, and to a lower range of acids, in the production of cow milk fat than in that of human milk fat. It may be said, in consequence, that human milk fat has more resemblance to many types of soft margarine fats than to the butterfat from cow's milk.

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CHAPTER IV*

THE COMPONENT ACIDS OF VEGETABLE FATS

In this chapter we shall be occupied for the most part with a very large number of fats from the seeds or fruit coats of the higher land flora. Before proceeding to deal with these it is logical to consider the comparatively few accounts to hand of the fatty acid components of fats present in the simpler plants, such as moulds, fungi, mosses, and other cryptogams. An interesting part of the plant kingdom—the aquatic flora—has already received attention, of course, in Chapter II (pp. 24–26), wherein the fats present in phytoplankton, algæ, and other aquatic vegetation were discussed.

Cryptogam Fats

The component acids of glycerides from several species of these simpler forms of vegetable life have been reported from time to time. Until recent years, they were usually given as a mixture of palmitic, stearic, oleic, and linoleic acids, but it has lately been shown that hexadecenoic acid is usually also fairly prominent.

Bacteria. The lipid matter of bacteria has received attention in the cases of tubercle bacilli and diphtheria bacteria. Those of tubercle and leprosy bacilli are mainly composed of waxes, and the extensive studies of Anderson [1] *et al.* have shown that the acidic components do not belong solely to the same series as the fatty acids of glycerides, but are to a considerable extent saturated acids possessing branched carbon chains (*cf.* Chap. IX, p. 394). Their melting points are much lower than those of the corresponding normal saturated aliphatic acids. Chargaff and Levine [90a] have reported that the acetone soluble lipids of *Phytomonas tumefaciens* contain palmitic, stearic, oleic, and 13 per cent. of a liquid saturated acid $C_{21}H_{42}O_2$, whilst Geiger and Anderson [90b] found that the phosphatides of this bacterium also contained a saturated acid liquid at ordinary temperatures.

Chargaff [2] found that diphtheria bacteria contain glyceridic fat, the component acids of which, in addition to about 30 per cent. of palmitic acid, consist mainly of Δ^9-hexadecenoic acid. The fat from typhoid bacilli from mice, according to Akasi,[91] contains 51 per cent. of saturated acids (chiefly palmitic, with some myristic and lauric) and 46 per cent. of unsaturated acids (chiefly oleic with some hexadecenoic acid).

Yeast. Yeast lipids have been studied by several workers, but no very clear-cut data have resulted, and apparently the systematic ester-fractionation procedure has not yet been applied to them. A typical study is that of Täufel [3] *et al.*, who apparently relied on determination of saturated acids by lead salt separation or Bertram oxidation, coupled with thiocyanogen and iodine values of the unsaturated acids. They reported that the specimen of yeast fat examined contained 3·3 per cent. of sterols and 16·3 per cent. of the hydrocarbon squalene, whilst the composition of the fatty acids (expressed as percentages of the latter) was as follows: lower acids volatile in steam 7·3, palmitic 13·4, stearic 8·3, oleic 66·9, and linoleic 4·1 per cent. That this is not the whole story is shown by the work of Newman and Anderson,[4] who showed that, whilst the saturated acids of baker's yeast were made up of 75 per cent. palmitic and 25 per cent. stearic acids, the unsaturated acids yielded on hydrogenation a mixture of 25 per cent. palmitic and 75 per cent. stearic acids. In other words, a quarter of the unsaturated acids, according to Newman and Anderson's data, must consist of hexadecenoic acid. In terms of Täufel's figures for the unsaturated acids, this would suggest that hexadecenoic acid accounts for about 18 per cent. of the total fatty acids. Since yeast fat may attain some industrial importance, it is to be anticipated that further and more complete studies of its composition may be made in the near future.

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* At the end of this chapter, owing to the very large number of references to individual determinations of component fatty acids in the tables, the literature references in the text are given separately from those in the tables (the latter being appended (for each table) following the textual references—" References to Table 47," etc.).

The content of glycerides and phosphatides in (dried) yeasts of various species was found by Rewald [85d] to be as follows:

Yeast	Glycerides (Per Cent.)	Phosphatides (Per Cent.)
Brewer's, bitter	1·2	0·8
,, debittered	1·9	2·2
,, autolysed	4·8	2·0
Vinegar	7·4	0·3

Rewald [85d] found that brewer's yeast phosphatides contain about 65–69 per cent. of lecithin and 35·3 per cent. of kephalin; Newman and Anderson [4] observed about 80 per cent. of lecithin with 20 per cent. of kephalin in the phosphatides of baker's yeast.

Moulds and fungi. The plasmodium of *Lycogala epidendrum* and of *Reticularia lycoperdon* contains respectively 37 per cent. and 23 per cent. of fatty matter; according to Kiesel,[5] the fatty acids present included 8–16 per cent. of palmitic, 70–77 per cent. of oleic, and 13–15 per cent. of linoleic acid.

Fairly recent and detailed analyses have been given for the component acids of the fats, present to the extent of about 10 per cent. of the dry weight, in three moulds, namely, *Penicillium javanicum* (Ward and Jamieson [6]), a species of *Citromyces* (Täufel, Thaler, and Schreyegg [7]), and *Oidium lactis* (Kaufmann and Schmidt [8]):

Component Acids	Penicillium Javanicum (Per Cent.)	Citromyces Sp. (Per Cent.)	Oidium Lactis (Per Cent.)
Palmitic	23·4	6·8	42·8
Stearic	9·4	11·8	
n-Tetracosanoic	0·8	—	
Oleic	34·6	40·7	41·2
Linoleic	31·8	40·7	11·8 *

* Also traces of linolenic acid and about 4 per cent. of hydroxy-acids.

A mould (probably a *Penicillium* species) grown on soya bean lecithin contained fat which, according to Hilditch and Meara,[92] included the following component acids: myristic 3·5, palmitic 40·5, stearic 8, arachidic 1, hexadecenoic 8, oleic 19, and linoleic 20 per cent. (wt.).

The fatty acids present in the fats of ergot (of barley) and maize blight have also received some notice. Ergot (*Secale cornutum*) contains from 15 to 30 per cent. of lipids, the acids of which have been examined by ester-fractionation by Baughman and Jamieson [9] and by Fiero [10] with the following results:

COMPONENT ACIDS	BAUGHMAN AND JAMIESON [9] (Per Cent.)	FIERO [10] (Per Cent.)
Myristic	0·3	3·0
Palmitic	21·6	25·0
Stearic	5·5	2·1
Arachidic	0·7	—
Oleic	63·1	20·9
Linoleic	8·8	13·2
Ricinoleic	—	35·8

The differences in the figures for unsaturated acids are remarkable, since it seems unlikely that ricinoleic acid would have been overlooked by Baughman and Jamieson; but Matthes and Schütz [11] have also stated that hydroxyoleic acids form 35 per cent. of the mixed acids of ergot oil. Jamieson [12] notes that various workers report appreciable (mostly high) acetyl values for ergot oil, ranging from 7 to 63, but were unable in most cases to isolate any definite hydroxy-acid; he adds that he is unable to account for the extreme variations shown in the acetyl values.

The fat (6 per cent. of the air-dried fungus) in maize blight (*Ustilago Zeæ*) was examined by the older methods in 1910 by Zellner,[13] who reported the usual 10–15 per cent. of saturated acids and 85–90 per cent. of oleic acid as the component acids.

The spores of a toadstool, *Amanita muscaria*, contain 1·4 per cent. of fat, the acids of which were stated by Heinisch and Zellner [14] to consist of about 10 per cent. of saturated (palmitic) and 90 per cent. of unsaturated (oleic) acids.

The pathogenic fungus *Monilia albicans* was observed by Peck and Hauser [93] to contain 5·3 per cent. of lipids (3 per cent. phosphatides, 97 per cent. acetone-soluble); the acetone-soluble portion contained 13·6 per cent. of sterols, whilst its fatty acids included palmitic 19·5, stearic 6·5, oleic 61 and linoleic 13 per cent. (wt.).

Clubmoss. The spores of *Lycopodium clavatum* contain about 50 per cent. of fat, the acids of which (apart from about 4 per cent. of myristic, palmitic, and stearic acids) were stated by Rathje [15] to consist, to the extent of over 90 per cent., of "lycopodic" acid, said to be an isomeric form of hexadecenoic acid. Riebsomer and Johnson [16] showed in 1933 that the *Lycopodium* spore-fat acids were made up of 55–60 per cent. of ordinary oleic acid with 30–35 per cent. of Δ^9-hexadecenoic acid, accompanied by smaller proportions of palmitic and linoleic acids.

Ferns. The fats in the spores of the larger ferns have not yet received much notice. The spores of the crested fern (*Aspidium dilatatum*, Polypodiaceæ), however, are stated by Maizite [94] to contain 35–40 per cent. of fat, with 14–21 per cent. of unsaponifiable matter (chiefly higher fatty alcohols), and fatty acids made up approximately of saturated 6, oleic 76 and linoleic 18 per cent. (wt.).

It is fairly evident that saturated acids may form from about 10 to 30 per cent. of the mixed acids of the fats of moulds, of fungi, and of the spores of mosses or ferns, and that palmitic acid is, as usual, the most abundant saturated acid, although stearic acid is sometimes present in fair quantity. The nature of the 70–90 per cent. of unsaturated acids is less certain. In most of the analyses it seems to be more or less arbitrarily assumed to be entirely oleic, or oleic with some linoleic acid. Even in the more detailed work of Jamieson, Täufel, or Fiero, it would appear that the possibility of the presence of hexadecenoic acid in appreciable proportions has not been considered. Since this acid has now been shown to be prominent in, for example, the fats of lycopodium spores and of yeast, it is probably safer to reserve judgment as to the exact nature of the unsaturated acids of many other similar fats until these have been re-investigated in still greater detail.

Phanerogam Fats

Fats occur in most parts of phanerogams—plants whose mode of reproduction is by seeds. During the period of growth they are present in the physiologically active cells of the leaf and stem systems, but, as a rule, form only a small proportion of the whole of the components. Moreover, they are accompanied by phosphatides (phosphatidic salts,[17] $C_3H_5(OR)_2.O.PO_3M$,* rather than actual phosphatides, $C_3H_5(OR)_2.O.PO(OH).O.[C_2H_4].N(CH_3)_3OH$), the amount being apparently of about the same order as that of the glycerides themselves.[18] In contrast to the glycerides associated with the growing plant, fats are also accumulated as reserve material in the maturing fruit and, in a few cases, in rhizomes or tubers. When they are deposited in this manner, they subsequently serve as a source of nutrition for the germinating seed (or, in the case of rhizome fats, during the commencing stages of growth in the following season). Very frequently fatty material forms a large part (25–50 per cent., or more) of the reserve material in the seed itself and, most often, reserve fat is practically wholly glyceride and is not accompanied by any appreciable proportion of phosphatidic compounds.

It is a natural consequence of the relative abundance of glycerides in fruit, and especially in seed, fats that our knowledge of their components is at present much more complete than in the case of leaf and similar fats. Seed fats can often be isolated in a pure condition, accompanied by only a few per cent. at most of non-glyceridic compounds; but in the leaf, for example, the glycerides may amount to little more than 1 per cent. or so of the dry weight, and their isolation and separation from ether-soluble plant pigments, as well as from the phosphatides which are also present, is a matter of great difficulty, especially if a sufficient amount of the glycerides for a complete examination is to be accumulated. To the plant physiologist and others interested in the chemical changes connected with the living plant cell the scarcity of data with reference to leaf and similar fats is unfortunate. On the other hand, the more extensive figures available for many fruit fats are of use not only to the biochemist but also to the technologist, since many seed fats are, of course, employed in the edible fat, soap, paint, and other industries.

Although, owing to the circumstances described in the preceding paragraph, it is not possible to present a properly balanced and comprehensive account of the component fatty acids of glycerides from all parts of plants, an attempt will be made to indicate the available data for each class (leaf, stem, root, fruit-coat, seed). The seed fats, in particular, will be discussed in groups, the classification depending upon the acids which are most prominent in each fat—the *major component acids* (*cf.* Chapter I, p. 8). Each group will therefore be prefaced by a sub-heading which indicates clearly both the chief major and minor component acids characteristic of the fats under consideration.

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* R = fatty acyl radical; M = metallic component (calcium, or, sometimes, magnesium).

A word may be added here with reference to the method which has been followed as regards utilisation of some of the older published data on the quantitative composition of mixed fatty acids from vegetable fats. Wherever possible, preference is given, in the succeeding tables, to analyses made, wholly or in part, by the more modern ester-fractionation process (denoted in the column " Method " by F). Many of the earlier data, especially when a fat contains only palmitic, stearic, oleic, and linoleic acids, are, however, probably well-founded (although some, unfortunately, are not so). The original literature has therefore been consulted in all possible cases and the methods employed by the investigators scrutinised ; when the latter have appeared trustworthy and the whole determination has been made on a quantitative basis the results have frequently been utilised in the tables which follow. In this way the extent of the information given on vegetable fat component acids has been amplified beyond that available from the modern analyses alone ; but, whilst care has been taken as far as possible to avoid inclusion of uncertain figures, it should be remembered that, in general, results obtained by methods not including separation by fractional distillation should be regarded as less certain than those in which ester-fractionation (F) has been employed.

The procedures (other than ester-fractionation) employed in individual cases are indicated as follows in the tables :

L. Separation of saturated acids by the lead salt-ether (Gusserow-Varrentrapp) or the lead salt-alcohol (Twitchell) processes or variants thereof ; or, in a few cases, by other metallic salts.

C. Preliminary resolution of mixed acids by crystallisation at low temperatures from acetone, ether, etc. (*cf.* Chapter XI, p. 471).

B. Estimation of saturated acids by the Bertram oxidation method.

H. Estimation of linolenic and linoleic acids by isolation and analysis of bromo-addition products (" hexabromides " in the case of linolenic acid).

K. Estimation of linolenic, linoleic, and oleic acids by the Kaufmann thiocyanogen method, employing Kaufmann's assumed values for linoleic and linolenic acids.

T. Estimation of linolenic, linoleic, and oleic acids from thiocyanogen values, employing the empirically determined values for linoleic and linolenic acids.

S. Estimation of linolenic and linoleic acids spectrographically after alkali-isomerisation to conjugated acids (Mitchell, Kraybill, and Zscheile ; Hilditch, Morton, and Riley [95]).

(Since the first edition of this book appeared, it has been shown that the thiocyanogen values originally assigned to linoleic and (especially) linolenic acid are far from correct, and the true values for the respective pure acids and their derivatives have been empirically determined.[96] This involves in many cases considerable differences in the resulting calculated compositions of unsaturated acids determined by the thiocyanogen method.

Wherever possible, therefore, the compositions of fatty acids, in the determination of which thiocyanogen values have been employed, recorded in this chapter (including Tables 47 to 59) have now been recalculated in terms of the more correct thiocyanogen values for linoleic and linolenic acids, and distinguished by the letter T in place of K.

The author hopes that this will meet with the approval of the investigators of the numerous fats, the data for which have been thus revised. Of the three alternatives, (*a*) revision in the light of the later information, (*b*) leaving figures known to be based on an erroneous form of calculation in their incorrect form, or (*c*) omitting the many data which thus stood in need of amendment, it was felt that the first (*a*) was the only satisfactory course.

The spectroscopic method S is, at the time of writing, only commencing to come into use ; but it will probably prove increasingly valuable as an alternative to the use of thiocyanogen values, in the determination of which difficulties have frequently been encountered and reported.)

For uniformity and ease of comparison, the data quoted in this chapter from the literature have, as a general rule, been transformed into *percentages of the total fatty acids*, in cases in which they were not originally published in this form (*cf.* Chapter I, p. 4, footnote). Data involving the computation of linolenic, linoleic, and oleic acids together, and also all data in which ester-fractionation was not employed, are in general given only to the nearest unit or half-unit per cent.

Leaf Fats

Major component acids: LINOLEIC, LINOLENIC, (OLEIC, PALMITIC).
Minor component acids: Stearic, cerotic.

The composition of leaf lipids has special interest in the cases of pasture grasses, but the complexity of these products has so far prevented any very detailed account of their components. In general, the dry matter in pasture grasses contains 4–6 per cent. of total lipids, made up of glycerides 1·5–4, waxes (chiefly *n*-hexacosanol) 0·5–1, other unsaponifiable matter (sitosterols) 0·5–1, phosphatides and phosphatidic acid salts (*cf.* pp. 137, 207) 0·2–0·3 per cent. (of total dry weight).

One of the more important attempts so far made to obtain quantitative information of the fatty acids of leaf glycerides is the work of Smith and Chibnall[19] on two grasses, cocksfoot (*Dactylis glomerata*) and perennial ryegrass (*Lolium perenne*) ; glycerides were present in these to the respective extents of 2·2 per cent. and 1·7 per cent. of the dry weights. The saturated acids (which consisted of a mixture of approximately 70 per cent. palmitic, 20 per cent. stearic, and 10 per cent. " cerotic " acids, the latter possibly emanating from small amounts of entrained grass waxes) were estimated by the Bertram oxidation and the Twitchell lead-salt processes, the latter giving lower results than the former. The mixed unsaturated acids were studied by the thiocyanogen method (K), accompanied by examination of the products of bromination and mild oxidation. Smith and Chibnall's figures suggest that palmitic acid forms about 10 per cent. of the mixed fatty acids in these two grass fats, and that, calculated from the iodine and thiocyanogen (K) values, the component acids of the leaf glycerides in both cocksfoot and perennial ryegrass are made up somewhat as follows : saturated 10–17, oleic 16–23, linoleic 30–21, and linolenic 44–39 per cent. (wt.).

Shorland has made similar general observations on the lipids present in New Zealand pasture grasses[97a] (chiefly ryegrass 55, Yorkshire fog 12, white clover 11, sweet vernal 10, and cocksfoot 5 per cent.), and has found the following average percentages (on the dry weight) of the lipid constituents of cocksfoot[97b] (*Dactylis glomerata*) to be glycerides 3·2, waxes

0·9, other unsaponifiable matter 1·0, phosphatides and phosphatidic acids 0·2 per cent. By ester-fractionation Shorland determined the component acids of the glyceride fraction to be myristic 1·4, palmitic 11·2, stearic 2·6, as arachidic 1·5, tetradecenoic 0·4, hexadecenoic 6·4, and unsaturated C_{18} 76·5(−5·1H) per cent. (wt.). These figures again suggest that octadecadienoic and octadecatrienoic acids are the major component acids of grass glyceride fats.

A subsequent ester-fractionation study by Jasperson and Burke[98] gave the following data for the component acids from a sample of mixed pasture grasses: saturated, C_{12} 2·9, C_{14} 3·3, C_{16} 9·4, C_{18} 1·5, C_{20} 0·7; unsaturated, C_{12} 0·3(−2H), C_{14} 0·4(−2H), C_{16} 3·0(−2H), C_{18} 78·5(−4·6H) per cent. (wt.). The unsaturated C_{18} acids appeared to include about 50 per cent. of linolenic with perhaps 15–25 per cent. of linoleic, the rest being oleic acid, a conclusion supported by the observations of Hilditch and Jasperson[98b] on the conjugated di- and tri-ene acids produced by alkali isomerisation of the unsaturated C_{18} acids of grass fat.

The only other leaf fats available for reference are single species from each of the families Cruciferæ, Labiatæ, and Chenopodiaceæ.

In the course of a study of cabbage (*Brassica oleracea*) leaf cytoplasm, Chibnall and Channon[20] found that about 1·7 per cent. of the leaf solids consisted of ether-soluble material, and showed that the glycerides present contained about 10 per cent. of saturated acids (about 70 per cent. of which was palmitic acid). The unsaturated acids contained much linoleic and a fair amount of linolenic acid; oleic acid was not identified and, if present, was evidently a minor component.

The dried leaves of peppermint (*Mentha aquatica*, Labiatæ) were found by Gordon[21] to contain nearly 5 per cent. of their weight of fatty components (as acids). A certain amount of volatile acids of low molecular weight is included in these, but the chief members present were palmitic, oleic, linoleic, and linolenic acids. Alkaline permanganate oxidation of the unsaturated acids yielded 2 parts of dihydroxystearic acid (m.p. 137°), 4 parts of tetrahydroxystearic acid (m.p. 173°), and 1 part of hexahydroxystearic acid (m.p. 202°), so that linoleic and oleic acids were present in quantity; although precise figures are not given, it would appear that the proportion of saturated to unsaturated acids was much greater than in the other leaf fats now under discussion.

Spinach leaves (from *Spinacea oleracea*, Chenopodiaceæ) have been similarly studied by Speer, Wise, Hart, and Heyl,[22] who obtained 260 grams of fatty acids from the neutral fat in 68 kilograms of dried leaves, or 0·4 per cent. The unsaturated acids were made up of about 30 per cent. oleic, 50 per cent. linoleic and 20 per cent. linolenic acids, and there was a small amount of saturated acids (palmitic and stearic, with small amounts of cerotic). According to Menke and Jacob,[99] about half of the lipids of spinach leaves consist of glycerides, the rest including 15–17 per cent. of wax alcohols, 2–7 per cent. of phosphatides, and 2–2·5 per cent. of sterols.

The fat of nettle (*Urtica dioica*) leaves contains very little (nil–5 per cent.) saturated acid, with 82–86 per cent. oleic acid as main component; the remaining 13–14 per cent. is linoleic, with perhaps some linolenic acid (Hilditch and Meara[92]).

Tsujimoto[100] identified linolenic acid in the leaf fats of clover, ginger, and three other plants, but did not detect it in the leaves of the black pine

(*Pinus thumbergii*), and Tang and Hsu [101] found lauric, oleic, linoleic, and linolenic acids in the leaves of *Leonorus sibiricus*.

Shorland[97c] has found the component acids of rape (*Brassica napus*) leaves to be saturated (chiefly palmitic) 15–16, tetradecenoic 0·5–0·7, hexadecatrienoic 17–11, and unsaturated C_{18} acids (of mean unsaturation over $-5H$) 67–72 per cent. (wt.). The presence of so much triethenoid C_{16} acid, and also the absence of erucic acid (the mono-ethenoid C_{22} acid which forms over 40 per cent. of the rape seed fatty acids), is noteworthy.

The scanty evidence thus available may be summed up in the statement that the leaf fats (from several very diverse families) so far examined show considerable similarity in their component acids. The latter consist mainly of the C_{18} unsaturated group, in which linoleic and linolenic (or, perhaps it is safer to say, octadecadienoic and octadecatrienoic) acids frequently predominate ; oleic acid is reported definitely in peppermint and spinach leaf fats, and as the chief component of nettle leaf fat, but is present only in minor amounts in other cases. The saturated members, which appear usually to form only about 10 per cent. of the whole, consist mainly of palmitic acid, with smaller amounts of stearic and (sometimes) cerotic acid, the latter probably emanating from small proportions of leaf waxes.

Bark Fats

Major component acids: OLEIC, LINOLEIC, (PALMITIC).
Minor component acids: Linolenic, stearic.

The component fatty acids of fat from the bark of trees or shrubs have been investigated in some detail in a few instances ; in most the main component appears to be oleic acid, but in one or two cases, saturated (palmitic and stearic) acids form over one-third of the whole, whilst in others they are almost negligible.

The bark of *Tilia cordata* (basswood, Tiliaceæ) was found by Pieraerts [23] to contain 2·3 per cent. of fat. The component acids of the latter (in which 7 per cent. of unsaponifiable matter was present) were mainly oleic (94 per cent.), with a little linoleic (4 per cent.) and palmitic or stearic (2 per cent.) acids.

Ruchkin [24] examined fat from the bark of the sea buckthorn (*Hippophaē Rhamnoides*, Elæagnaceæ), in which it was present to the extent of 3 per cent., and reported that it contained 37·4 per cent. of saturated (palmitic and stearic) acids and 62·6 per cent. of unsaturated (oleic) acid.

Dieterle and Dorner [25] have reported that the bark fat of the hawthorn (*Cratægus oxyacantha*, Rosaceæ) also contains oleic, palmitic, stearic, and myristic amongst the higher fatty acids.

The lipids of the sugar cane (" sugar cane wax ") were found by Vidyarthi and Narasingarao [103] to contain about 44 per cent. of unsaponifiable matter : this included about 80 per cent. of mellisyl alcohol, about 10 per cent. of sterols (brassicasterol, stigmasterol and sitosterol), and about 5 per cent. of *n*-pentatriacontane, $C_{35}H_{72}$. The component fatty acids present in combination (chiefly as *wax esters*) were found by ester-fractionation to be palmitic 29·2, stearic 23·6, arachidic 3·5, and oleic 43·7 per cent. (wt.).

Reference is also due, whilst discussing bark and stem fats, to the industrial product known as " talloel," a dark-coloured liquid resinous product obtained to some extent as a by-product in the manufacture of rosin, but mainly from the " black liquor " produced as a residue in the manufacture of paper from wood pulp. This material, representing some of the fats present in the spruce or other coniferous wood employed in the paper industry, is said to have a possible annual production in the United States of 150,000–200,000 tons.[26] Somewhat variant statements as to the acidic components of talloel have been given by Becher,[27] Niesen,[98] and Anderson and Wheeler,[121] as follows :

TALLOEL	ACID CONTENT		COMPONENT FATTY ACIDS (PER CENT. WT.)			
	ROSIN	FATTY	SATURATED	OLEIC	LINOLEIC	LINOLENIC
Crude [27]	ca. 30	ca. 60				
Distilled [27]	ca. 12	ca. 85				
Distilled [28]	33	67	—	15	79	6
Crude [121]	46–38	26–45	7	45	48	—*
Refined [121]	32	61				

* The saturated acids were chiefly palmitic acid, and about 11 per cent. of conjugated octadecadienoic acid (probably formed from linoleic acid during processing of the wood pulp) was present.

Root Fats

Major component acids: OLEIC, PALMITIC, (LINOLEIC).
Minor component acids: Stearic, arachidic, etc.

The most conspicuous example of a fatty oil derived from the roots of a plant is probably sedge (or chufa) oil, which forms 20–30 per cent. of the substance of the small tubers of the tropical sedge (*Cyperus esculentus*, Cyperaceæ). This oil has been examined by the modern methods by Baughman and Jamieson,[29] who found that the component fatty acids were myristic (traces), palmitic (12·2), stearic (5·4), arachidic (0·5), lignoceric (0·3), oleic (75·5), and linoleic (6·1 per cent.) ; Pieraerts [30] has also reported that oleic acid forms 80 per cent. of the mixed acids, but states that the remaining 20 per cent. is chiefly myristic, with a little palmitic, acid. Josephs [31] found 14·4 per cent. of oil in chufa tubers, the component acids being saturated (15), oleic (68), and linoleic (17 per cent.).

The component acids of poke root oil, from *Phytolacca americana* (Phytolaccaceæ) are, according to an analysis by Goldstein and Jenkins,[32] somewhat as follows : palmitic 11, stearic 2, arachidic 6, and oleic about 80 per cent.

Mangel roots (*Beta rapa vulgaris*, Chenopodiaceæ), according to Neville,[33] contain about 7 per cent. of fatty oil, the component acids of which consist of oleic 57, palmitic 14, and erucic 29 per cent. ; whilst senega root (*Polygala senega*, Polygalaceæ) was observed by Schröder [34] to contain 5–9 per cent. of oil, the acids of which were oleic (ca. 90 per cent.) and palmitic (ca. 10 per cent.). An oil from the tubers of the Japanese *Pinellia tuberifera* (Araceæ) seems, according to Nakayama,[35] to be very similar in composition to senega root oil.

With the exception of the reported presence of 30 per cent. of erucic acid in the oil of mangels, it will be observed that all five root oils contain, roughly speaking, a mixture of fatty acids made up of about 80–90 per cent. of unsaturated (oleic) and 10–20 per cent. of saturated (mainly palmitic) acids.

It should be noted that, up to the present (with the one exception just noted), the only major components of fatty oils from leaves, stems, and roots of plants, or from fungi, have been found to be oleic and palmitic acids, with linoleic (and linolenic) acids in addition to, or perhaps even replacing, oleic acid in leaf fats.

Lipids of Petals and Stamens

Little has yet been reported on the lipids of flowers, but Rewald [85e] has observed the following percentages of glycerides and phosphatides in dry petals and stamens of different species :

	GLYCERIDES (Per Cent.)	PHOSPHATIDES (Per Cent.)
Daffodil petals	5·8	1·4
Dandelion petals	ca. 6	3·0
„ stamens	9·1	2·9
Poppy petals	3·4	0·7
„ stamens	6·3	1·4
„ seeds (green, young)	6·7	2·8
Rose petals	2·9	3·5
Tulip petals	3·2	1·8
„ stamens	1·8	2·2

The phosphatides thus nearly always formed over 20 per cent., and sometimes as much as 45–50 per cent., of the total lipids. The iodine values of the glycerides in the petals, stamens, and undeveloped seeds of the poppy were respectively 88, 97, and 95, compared with about 140 for the ripened seeds.

It may be mentioned here that the fat in the flower petals of poppies (*Papaver Rheas*) and of *Arnica montana* has been stated to contain mainly oleic acid, together with some palmitic and minor amounts of stearic and lower saturated acids.[102a] From the petals of *Matricaria* flowers the methyl ester of a highly unsaturated acid, $C_{10}H_8O_2$, has been isolated [102b] ; the acid is possibly $CH_3.CH{:}CH.C{\vdots}C.C{\vdots}C.CH{:}CH.COOH$.

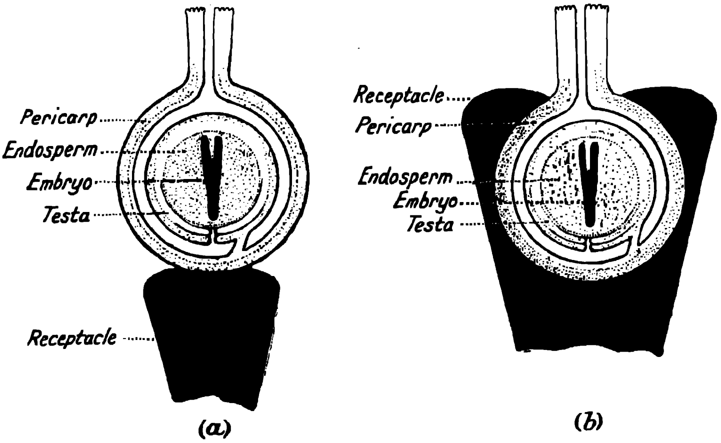
Fruit Fats

It has already been said that far more information is available with reference to the component acids of fruit fats than is the case in those of fats from the rest of the organs of plants. In classifying this mass of data it will be useful to consider first the many cases in which the major components are practically confined (as in leaf, stem, and root fats) to oleic, linoleic, and palmitic acids. This will lead us, in the first place, to the category of fruit-coat fats, which appear to be made up almost exclusively of these acids, although in quite a number of cases the proportion of linoleic acid is not great, and in some cases subordinate amounts of stearic acid are found. Then, in the seed fats, it will be convenient first to deal with the numerous and important groups in which, again, only these acids occur as major components.

It may not be out of place here to describe very briefly the various formations which are met with in different fruits. In the flower the ovary is attached to the extremity of the stalk (peduncle) bearing the flower.

This apex, termed the *receptacle*, may be extremely small, but is often more or less elongated, thickened or otherwise enlarged; it may be connected with the ovary as indicated in Fig. 1 (*a*), when the ovary is said to be *superior* or *free*, or it may partially surround the ovary in such a way that it adheres to it above the level of the insertion of the lowest ovule, in which case the ovary is described as *inferior* or *adherent* (Fig. 1 (*b*)). Figs. 1 (*a*) and 1 (*b*) actually refer to the development of the fruit after fertilisation has taken place. In flowers with a superior ovary the fruit itself is seen distinct from the receptacle and consists essentially of a *fruit-wall* or *pericarp* enclosing the seed.

The seed consists of the *embryo* or *germ* which may either fill or almost fill the seed cavity or be set in a mass of reserve food tissue termed the *endosperm* or "*albumen*"; the food reserves in the endosperm include carbohydrates, proteins, and fats in varying proportions. If, during development of the seed, the embryo grows so as to absorb all the endosperm (the mature seed then being termed non-endospermic or exalbuminous), the food reserves are then in the embryo which in this case makes close contact with the *testa* or seed coat. The *testa* or outer covering of the seed may be a thin skin or it may be hard and woody.



(*a*) (*b*)

Fig. 1.

Seed fats, as discussed in this book, are fats present in the endosperm or embryo of the seed. In a few cases reference will also be made to fats present in the seed covering and these will be termed *testa fats*.

The seed is connected to the inner side of the pericarp (originally the placenta of the ovary) by a short stalk or *funicle*, which sometimes (e.g. in the mace of *Myristica* species) carries a fleshy appendage termed an *arillus*, which may contain fat.

Returning now to the *fruit-wall* or *pericarp*, we find in the first place that this, the developed ovary enclosing the ripened seed, may also often be divided into three zones: (i) an exterior, relatively hard, skin or rind (*epicarp*) enclosing (ii) a more or less fleshy or pulpy substance (*mesocarp*) whilst in some cases there is, between the latter and the seed or seeds, (iii) a thin inner skin known as the *endocarp*.

Except in the class of *Gymnosperms* (e.g. the Coniferæ), in which the seeds are naked and without any real pericarp, this fruit-wall system is present whether the ovary is superior or inferior; but in the latter case (Fig. 1 (*b*)) the *receptacle* frequently, in the mature fruit, acquires some or most of the characteristics of the pericarp. The outer limits of the pericarp and the inner zones of the receptacle may lose their identity or become fused to a large degree; or the ripened receptacle may become fleshy whilst the pericarp, or the inner part thereof, becomes hard and woody.

Fats are found indifferently in either type of *Angiosperm* fruit, that is, in true pericarp, receptacle, or in pericarp and receptacle. Often these have been indiscriminately termed "pericarp fats" but, for purposes of convenience in these pages, the term "*fruit-coat fat*" will be employed to denote *fats from parts of a fruit other than the seed* (*embryo, endosperm, or testa*). Fruit-coat fats, thus defined, may be found, in different instances, either exclusively in the pericarp or in the receptacle, or in both of these, or occasionally, in arils attached to the funicle.

Fruit-coat Fats

Major component acids: PALMITIC, OLEIC, LINOLEIC.
Minor component acids: Myristic, stearic, (linolenic).

The fleshy or succulent part of many fruits contains more or less fatty oil. In some cases the proportion of fat is considerable and the fruits have become, in consequence, sources of edible oils or of raw material for the fat industries; the most familiar examples are olive oil and the red palm oil of *Elæis guineensis*.

Quite a number of determinations of the component acids of fruit-coat fats have been made within recent years, mostly by the ester-fractionation method, of which many deal with different varieties of one oil (palm or olive). All the available figures, it is believed, will be found in Table 47; the data are arranged approximately in descending order of the contents of palmitic acid.

In the cases of the Palmæ, Myristicaceæ, and Lauraceæ (as will be seen later, pp. 198–204) the specific composition of the seed fats is such (owing to the small proportion of oleic acid and the large proportions of acids (lauric, myristic) of only medium molecular weight) that the simple saponification and iodine values of the fats are quite different from those of the fruit-coat fats included in Table 47 (pp. 146, 147). This may be illustrated by the respective values for the fruit-coat and seed fats of the West African oil palm (*Elæis guineensis*):

	SAPONIFICATION VALUE	IODINE VALUE
Palm oil (fruit-coat)	198–205	52–58
Palm kernel oil (seed)	243–250	15–20

Some evidence for other fruit-coat fats of a number of members of the palm family, and for the arillus fats of two species of *Myristica*, may therefore be derived from a comparison of their saponification and iodine values. These additional data are given in Table 47A.

TABLE 47. *COMPONENT ACIDS (WTS. PER CENT.) OF FRUIT-COAT FATS*

Major component acids: PALMITIC, OLEIC, LINOLEIC.
Minor component acids: Myristic, stearic, (linolenic).

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.)		SATURATED		UNSATURATED		METHOD	OBSERVERS
			LAURIC	C_{14}	PALMITIC	C_{18}	OLEIC	LINOLEIC		
ANACARDIACEÆ										
Rhus succedanea	Sumach	Japan, etc.		—	77	5	12	Trace (*a*)	F	Tsujimoto[1]
		,,		1·9	67·5	11·6	13·6	— (*a′*)	F	Schuette and Christenson[44]
EUPHORBIACEÆ										
Stillingia sebifera	Stillingia, Chinese vegetable tallow.	China		5·8 (*b*)	69·6	3·1	20·7	—	F	Hilditch and Priestman[2]
		,,		3·6 (*b*)	57·6	1·8	34·5	—	F	,, ,, [2]
		Florida		3·7 (*b*)	66·3	1·2	26·9	—	F	,, ,, [2]
PALMÆ										
Elæis guineensis	Oil palm	West Africa		1·0	35·5	8·5	48·0	7·0	F	Armstrong and Allan[3]
	Plantation Oils	Belgian Congo		0·5	41·0	5·2 (*c*)	47·6	5·6	F	Jamieson and McKinney[4]
	,, ,,	,, ,,		1·2	43·0	4·4	40·2	11·2	F	Hilditch and (Miss) Jones[5]
	,, ,,	Malaya		2·5	40·8	3·6	45·2	7·9	F	,, ,, [5]
	,, ,,	Sumatra		0·6	43·8	2·9	43·1	9·5	F	Jamieson and Gertler[6]
	,, ,,	,,		2·5	41·8	4·2	42·1	9·4	F	Dean and Hilditch[7]
	,, ,,	,,		1·5	42·9	4·7	39·8	11·3	F	Steger and van Loon[8]
	Native Oils	Sierra Leone		2·0	35·9	6·1	48·0	8·0	F	Dean and Hilditch[7]
	,, ,,	Liberia, Sherbro		1·6	35·0	5·3	50·1	8·0	F	,, ,, [7]
	,, ,,	,, Grand Bassa		2·0	33·5	6·4	50·5	7·6	F	,, ,, [7]
	,, ,,	,, Cape Palmas		1·6	32·3	5·5	52·4	8·2	F	,, ,, [7]
	,, ,,	Ivory Coast, Drewin		2·3	34·3	5·6	49·5	8·3	F	Hilditch and (Miss) Jones[5]
	,, ,,	,, ,,		2·2	35·3	5·2	52·3	5·0	F	,, ,, ,, [9]
	,, ,,	Gold Coast, Takoradi		1·9	40·8	4·9	43·3	9·1	F	Dean and Hilditch[7]
	,, ,,	Nigeria, Lagos		—	47·0	1·0	50·0	2·0	F	Heiduschka and Endler[10]
	,, ,,	,, ,,		1·2	39·6	5·8	42·4	11·0	F	Dean and Hilditch[7]
	,, ,,	,, ,,		2·7	42·5	3·4	40·9	10·5	F	,, ,, [7]
	,, ,,	,, Benin		4·5	37·5	4·2	47·3	6·5	F	Hilditch and (Miss) Jones[9]
	,, ,,	,, Bonny Old Calabar		4·1	40·1	4·4	41·5	9·9	F	,, ,, ,, [9]
	,, ,,	Niger		5·9	39·3	2·2	42·7	9·9	F	,, ,, ,, [9]
	,, ,,	Cameroons		1·0	38·9	5·9	43·9	10·3	F	,, ,, ,, [5]
Œnocarpus pataua	Patua palm oil	Brazil		—	9·3	5·9	81·1	3·6	F	Jamieson and McKinney[11]
CARYOCARACEÆ										
Caryocar villosum	Piqui-a oil	Malaya		1·5	41·2	0·8	53·9	2·6	F	Hilditch and Rigg[12]
MELIACEÆ										
Trichilia emetica		Sudan			←—— 44 ——→		29	27	B, T	Henry and Grindley[45]
STERCULIACEÆ										
Sterculia fœtida	"Java olive"	Java			←—— ca. 40 ——→		← ca. 60 →		B	Steger and van Loon[46]
,, *parviflora*		Malaya		2·3	27·6	9·0 (*f*)	37·6	22·2	F	Hilditch and Meara[47]
,, *tomentosa*		Sudan			←—— 32 ——→		63	5	B, T	Henry and Grindley[45]
Theobroma cacao	Cacao bean shell	Tropics		—	← 51–56 →		33–35	16–9	B, T	Bauer and Seber[13]
BURSERACEAE										
Dacryodes rostrata *	"Java almond"	Malaya		—	33·9	2·7	59·3	4·1	F	Hilditch and Stainsby[14] *
MYRICACEÆ										
Myrica mexicana	Myrtle, bayberry	Central America, etc.		61·1	37·5	—	1·4	—	F	Jamieson, McKinney and Gertler[15]
LAURACEÆ										
Laurus nobilis	Laurel, bay	Mediterranean coasts	—	—	24	—	57	19	?	Wallrabe[16]
	,, ,,	,, ,,	2·7	—	20·3	—	63·0	14·0	F	Collin[17]
Neolitsea involucrata	Wild cinnamon	Ceylon	10·2	—	28·2	3·1	48·2	10·3	F	Gunde and Hilditch[18]
Actinodaphne Hookeri		India	33	—	—	—	56	— (*d*)		Puntambekar and Krishna[19]
Persea gratissima	Avocado pear	Sub-tropics	—	—	7·2	0·6	80·9	11·3	F	Jamieson, Baughman and Hann[20]
	,, ,,	Puerto Rico	—	2·2	26·1	0·6	64·8	6·3	F	Asenjo and Goyco[48]
CELASTRACEÆ										
Celastrus paniculatus		India		3·0	26·2	4·0	36	8 (*e*)	F, T	Gunde and Hilditch[21]
VALERIANACEÆ										
Valerianella olitorea	Corn salad	Europe			←—— 20·5 ——→		5·5	74 (*f*)	L, T	Steger and van Loon[22]
CAPRIFOLIACEÆ										
Sambucus racemosa	Elderberry	General		—	23	—	71	6	L	Byers and Hopkins[23]
OLEACEÆ										
Olea europæa, sativa	Olive oil	Californian		—	7·0	2·3 (*g*)	85·8	4·7	F	Jamieson and Baughman[24]
		Corsica		—	9·4	2·0 (*g*)	84·5	4·0	F	,, ,, [25]
		Tunisian		0·1	14·7	2·4 (*g*)	70·3	12·2	F	,, ,, [26]
		Spanish		0·2	9·5	1·4 (*g*)	81·6	7·0	F	,, ,, [27]
		Italian (Tuscany)		1·1	9·7	1·0 (*g*)	79·8	7·5	F	Hilditch and Jones[28]
		,, ,,		1·2	15·6	2·0	64·6	15·0	F	Gunde and Hilditch[49]
		Palestine		0·5	10·0	3·3 (*g*)	77·5	8·6	F	Hilditch and Thompson[29]
		Mediterranean Islands—								
		Arcangelo		0·9	19·7	—	68·7	10·7	?	Brandonisio[30]
		Afando		0·4	18·7	—	67·6	13·3	?	,,
		Alærma		0·6	18·4	—	68·5	12·5	?	,,
		Cos		0·4	17·1	—	68·8	13·7	?	,,
		Peveragno		0·8	19·1	—	69·5	10·6	?	,,
		Rhodes		—	19·7	0·3	69·6	10·4	?	,,
ELÆAGNACEÆ										
Hippophaë Rhamnoides	Sea buckthorn	Siberia		—	←— 12·3 —→		75·2	12·5		Ruchkin[31]

* This was published as the fruit-coat fat of *Sterculia fœtida*, but the fruits have subsequently been found not to be those of this plant, but of *Dacryodes rostrata*, a plant known with related *Canarium* sp. as "Java almond."

(*a*) 5–6 per cent. dibasic acids of C_{22} and C_{23} series.
(*a′*) 5·3 per cent. dibasic acids of C_{23} series.
(*b*) Small amounts of lauric or lower acid (1–2·5 per cent.).
(*c*) 0·1 per cent. lignoceric acid.
(*d*) Also 11 per cent. resin acids.
(*e*) Also 23 per cent. linolenic acid.
(*f*) Also 1·3 per cent. arachidic acid.
(*g*) Traces of arachidic acid.
(*h*) Also 1·6 per cent. hexadecenoic acid.

TABLE 47A. *SAPONIFICATION AND IODINE VALUES OF SOME FRUIT-COAT FATS FOR WHICH DETAILED DATA ARE LACKING*

			SAP. VALUE	IODINE VALUE
PALMÆ				
Acrocomia sclerocarpa	Gru-gru	West Indies, South America	190	77 [32]
Astrocaryum aculeatum syn. *vulgare.*	Aouara, Tucum	South America	220	46 [32]
Astrocaryum Jauari	Awarra	Brazil	196	68 [33]
„ *segregatum.*		Guiana	197	70 [34]
„ *Tucuma*	Tucuma	West Indies, Central America	202	40 [35]
Attalea cohune	Cohune	Honduras	197–203	65–75 [36]
Elæis melanococca	Cayau, Noli palm	Central and South America	197–199	78–88 [37]
Jessenia polycarpa		Brazil, Columbia	190	74 [38]
Maximiliana regia	Cokerite palm	Brazil, Guiana	207–211	51–56 [39]
Œnocarpus distichus	Batava palm	Central and South America	209	55 [40]
Oreodoxa regia		Central America	192	75 [41]
Raphia ruffia		Madagascar	197	? [42]
MYRISTICACEÆ				
Myristica fragrans		East Indies	170–173	78–80 [43]
„ *malabarica*		„ „	189–191	51–53 [43]

The material in Tables 47 and 47A invites comment from several aspects. In the first place, the general characteristics of all the fruit-coat fats are the same: the main components are palmitic and oleic acids, the former reaching 70 per cent. or more of the whole in *Rhus* and *Stillingia* fruit-coat fats, about 40 per cent. in palm oil, and falling to somewhat less than 10 per cent. in other cases, whilst oleic acid varies from negligible proportions in the myrtle and Rhus " waxes " to 40–50 per cent. in palm oils and 75–80 per cent. in the more liquid oils such as olive or elderberry. With the exception of linoleic acid, other component acids rarely form more than 2–5 per cent. of the mixed acids.

The only exceptions to the last statement are the fruit-coat fats of *Myrica mexicana* and of some Lauraceæ fruits. In the *Myrica* fruit-coat fat myristic acid (61 per cent.) is the major component (with 37·5 per cent. palmitic acid); earlier workers[36] have described this fat as consisting almost entirely of tripalmitin, but the detailed figures quoted are from an exceptionally reliable and recent source, and it may be, therefore, that the myrtle pulp fat is a partial exception to a more generally followed rule.

The seed fats of some members of the Lauraceæ contain exceedingly high proportions of lauric acid (90 per cent. or more, *cf.* p. 200), and, from the few analyses available it seems that in these plants the fruit-coat fats also contain a certain amount of combined lauric acid. The amounts are, however, small in comparison with those in the corresponding seed fats, and, moreover, palmitic acid is usually present in considerably larger quantities than lauric acid in these fruit-coat fats, whilst oleic acid (a very minor component of the seed fats) forms 50 per cent. or more of the fruit-coat fatty acids.

In the next place, it is fortunate that, although the data only cover members of eleven botanical families, the seed fats of the latter are so diverse in composition that we are presented with a very striking series of fruit-coat fats qualitatively similar in component acids, coupled with corresponding seed fats ranging from almost saturated to extremely unsaturated, and containing a wide variety of saturated fatty acids. This is clearly illustrated by the summary in Table 48.

We shall find, when discussing the component acids of seed fats, that a wide variety of fatty acids enters into their composition, but that the mixture found within the limits of any given botanical family is nearly always qualitatively, and to some extent quantitatively, the same. Thus the proportions and kinds of fatty acids present in palm kernel oil are closely simulated in the other Palmæ seed fats (*Areca catechu*, *Astrocaryum* species, *Attalea* species, *Cocos nucifera*, etc.) which have been submitted to detailed analysis and, again, the saponification and iodine values of other Palmæ seed fats indicate similar agreement in their component fatty acids with the foregoing, as will be seen from Table 48A.

TABLE 48A

	SEED FAT		FRUIT-COAT FAT	
	SAPONIFICATION VALUE	IODINE VALUE	SAPONIFICATION VALUE	IODINE VALUE
Acrocomia sclerocarpa	237–255	16–30	190	77
Astrocaryum aculeatum	240–249	10–14	220	46
,, *Jauari*	242	13–15	196	68
,, *segregatum*	238	17	197	70
,, *Tucuma*	250	9	202	40
Attalea cohune	252–256	11–13	197–203	65–75
Elæis melanococca	234	27–28	197–199	78–88
Maximiliana regia	240–253	7–16	207–211	51–56

Thus, whilst seed fats of the Palmæ, Myristicaceæ, and Lauraceæ usually contain very large amounts of lauric and/or myristic acids, their fruit-coat fats are mainly made up of palmitic, oleic, and linoleic acids in varying proportions.

There is therefore no apparent connection between the general nature of the component acids of fruit-coat and seed fats. Sometimes, as in the fruits of the olive, piqui-a, or cacao plants, the seed fat is closely similar to the fruit-coat fat, but this seems to be exceptional rather than otherwise. In six or seven of the plant species illustrated in Table 48, however, it may be noticed that the fruit-coat and seed fats contain about the same proportion of palmitic acid. A fruit-coat fat of comparatively high melting point (i.e. relatively rich in combined palmitic acid) may be associated with a highly unsaturated liquid seed fat (*Stillingia*) or an almost saturated solid fat (Palmæ); liquid (" non-drying " oil) fruit-coat fats, equally, are found in instances where the seed fats are soft solids and their component acids mainly saturated (Lauraceæ, Myristicaceæ), or where the seed fats are " drying " oils (elderberry, buckthorn); and so on. It is becoming fairly clear, however, that, whereas seed fats contain a wide range of specific component acids according to their botanical origin, fruit-coat fats almost invariably include only palmitic and oleic, with occasionally linoleic, amongst their major component acids.

It will be observed that, in spite of the general constancy in the qualitative nature of their components, fruit-coat fats vary almost as widely as seed fats in their physical properties. Whereas, however, relatively high melting point in a seed fat is almost always due to the presence in quantity of

TABLE 48. *CONTRASTS IN COMPOSITION OF FRUIT-COAT AND SEED FATS FROM THE SAME FRUIT*

		FRUIT-COAT FAT COMPONENT ACIDS				SEED FAT COMPONENT ACIDS				
		LAURIC	PALMITIC	OLEIC	LINOLEIC	LAURIC	PALMITIC	OLEIC	LINOLEIC	OTHERS
ANACARDIACEÆ	*Rhus* sp.	—	77	12	Trace	—	Small	Much	Much	—
EUPHORBIACEÆ	*Stillingia sebifera* †	—	60–70	20–35	—	—	6	16	46	29 per cent. linolenic.
PALMÆ	*Elæis guineensis*	—	35–40	40–50	5-11	47	9	18	1	14 per cent. myristic, etc.
CARYOCARACEÆ	*Caryocar villosum*	—	41	54	3	—	48	46	3	—
STERCULIACEÆ	*Theobroma cacao*	—	ca. 50 ‡	ca. 35	ca. 10	—	ca. 60 ‡	ca. 37	ca. 2	—
BURSERACEÆ	*Dacryodes rostrata*	—	34	59	4	—	11	44	3	40 per cent. stearic.
LAURACEÆ	*Laurus nobilis*	3	20	63	14	43	6	32	18	—
	Neolitsea involucrata	10	28	48	10	86	—	4	3	—
CELASTRACEÆ	*Celastrus paniculatus*	—	26	36	8*	—	22	22	35	16 per cent. linolenic.
CAPRIFOLIACEÆ	*Sambucus racemosa*	—	23	71	6	—	23	45	24	8 per cent. linolenic.
OLEACEÆ	*Olea europæa*	—	7-15	70–85	4–12	—	6	83	7	4 per cent. stearic.
ELÆAGNACEÆ	*Hippophaē Rhamnoides*	—	12	75	12	—	11	41	33	15 per cent. linolenic.
MYRISTICACEÆ	*Myristica officinalis*	—	?	ca. 80	?	—	10	10	—	77 per cent. myristic.

* Also 23 per cent. linolenic acid.

† Syn. *Sapium sebiferum*.

‡ Total saturated acids (palmitic and stearic).

saturated acids other than palmitic acid, the different consistencies of fruit-coat fats at the ordinary temperature are solely controlled in all the foregoing instances by variation in the respective proportions of palmitic and oleic (with linoleic) acids. The physical properties of either fruit-coat or seed fats are, of course, in a sense accidental, in that they are determined by the component fatty acids and glyceride structure ; the causes which in turn determine the kind and amount of the various acids and their combination into natural glycerides of specific structure remain unknown.

The data in Table 47 allow us, in the cases of olive and palm oils (and possibly Stillingia tallow), to examine to some extent the degree of constancy of composition of oils of a given species.

The palm oils offer the best scope for comparison, in view of the number of specimens examined, and here a minor, but quite definite, variation in the proportion of palmitic acid is to be connected with the locality in which the oil palm is grown. Roughly speaking, the oils gathered from palms grown east of about longitude 4–6° W. (i.e. from the Ivory and Gold Coasts eastwards) all contain about 40 per cent. of palmitic, about 43–44 per cent. of oleic, and about 9–10 per cent. of linoleic acid ; but as the oils are derived from more westerly parts of the coast (Liberia and Sierra Leone) another type is met with, characterised by a lower content of palmitic acid (about 35 per cent.) and correspondingly higher oleic acid (about 50 per cent.). The cause of this variation is unknown ; it was first noticed in 1928 by Dyke,[37] who pointed out that the setting point of the mixed fatty acids of the oils from the more westerly regions was slightly lower (ca. 41° C.) than that (ca. 44° C.) of Gold Coast or Nigerian oils. The geographical difference is one of longitude, not latitude, and it seems unlikely that climatic variations will come into consideration ; there might be differences in the soil or, perhaps more probably, the oil palm in the western districts may be a different variety from that indigenous to the Gold Coast and the Niger.

The plantation oils from the Belgian Congo, Malaya, and Sumatra all show close similarity between themselves and also with the native oils of the Gold Coast and Niger regions ; this is probably in consequence of seed having been originally drawn from the variety indigenous to one or other of these districts.

The olive oils appear to fall into two groups. Most olive oils from Italy, Spain, Asia Minor, or California agree closely in containing about 9–10 per cent. palmitic acid, about 2 per cent. of stearic acid, and not more than about 7 per cent. of linoleic acid ; these oils are so similar in composition that, for the acids mentioned, the variations are not far outside the limits of experimental error of the ester-fractionation method. The oleic acid content lies between the extremes of 78 and 86 per cent. (in all but two of the analyses between 77·5 and 81·6 per cent.).

On the other hand, the Mediterranean (Dodecanese) Island oils examined by Brandonisio,[38] the Tunisian oil analysed by Jamieson and Baughman,[39] and an oil reputedly of Italian (Tuscany) origin studied by Gunde and Hilditch [104] show oleic acid contents of 70–65 per cent., with 10–15 per cent. of linoleic acid and 15 per cent. or more of palmitic acid ; the palmitic acid figures given by Brandonisio (17–19·7 per cent.) are exceptionally high. The latter author suggests that, contrary to what is often observed in seed fats, the olive fruit-coat oils contain more linoleic acid when grown in warmer climates. The division of the olive oils, by their fatty acid compositions, into these two well-defined groups suggests, however, that the difference may be due to a difference in species or variety of the olive tree, rather than to climatic or geographical influences.

Finally, it may be pointed out that the fruit-coat fat of sumach (*Rhus* sp.) berries, commonly known as " Japan wax," is unusual not only in its extremely high content of palmitic glycerides but also because it contains up to 6 per cent. of saturated dibasic acids, first reported by Eberhardt [40] as $C_{18}H_{36}(CO_2H)_2$ and later by Geitel and van der Want [41] as " Japanic acid," $C_{20}H_{40}(CO_2H)_2$. In 1931 Tsujimoto [42] showed that the dibasic acids were a mixture of at least two homologues, $C_{21}H_{42}(CO_2H)_2$, m.p. 123·5°, and $C_{20}H_{40}(CO_2H)_2$. The presence of these acids (which, incidentally, belong to the normal series $COOH \, . \, [CH_2]_n.COOH$) is held to confer on " Japan wax " its characteristic properties of toughness and ability to be kneaded without crumbling.

Seed Fats

A very large number of seed fats contain, as major component acids, only those—palmitic, oleic, linoleic, and sometimes linolenic—which have been found to characterise fats from parts of plants other than the seed. Many others, again, in addition to one or more of the acids mentioned, have as major components one or more distinctive acids, either saturated or unsaturated. It is therefore possible to group most seed fats according to their predominating component acids, although in a minority of instances this method of grouping at present becomes somewhat ill-defined, for example, in consequence of more than one of the more usual mixtures of major components occurring in the same seed fats (those of the Leguminosæ family, pp. 188, 189, form a well-marked case in point). As already mentioned in Chapter I (p. 14), grouping of seed fats according to their chief component acids leads at once to the circumstance that seed fats of plants in the same botanical family usually fall in the same group, and often show great similarity in their composition.

It should be clearly understood, however, that the grouping of seed fats adopted in this book is *primarily* based upon *similarities in their major component acids*. When, however, some irregularity in fatty acid composition interferes with this mode of classification, it is usually discernible that here also the specific variations in any given instance are again in seed fats of a particular botanical family ; in such cases it is for the time being convenient to adopt a *secondary* classification subordinate to the main grouping, and to consider the seed fats of the *plant families* concerned in these instances.

The seed fats in which only palmitic, oleic, linoleic, and/or linolenic acids are major components will be discussed first of all. These may be subdivided into the following groups :

I. Those in which linoleic and linolenic acids predominate.
II. „ „ „ oleic and linoleic „ „
III. „ „ „ oleic and palmitic „ „

Groups I, II, and III, of course, correspond approximately with the empirical divisions of " drying," " semi-drying," and " non-drying " oils and, indeed, most of the more familiar of these oils will be found in these three groups.

There are a number of fats, however, in which linoleic acid is prominent, which also contain specific saturated acids, and there are others in which linoleic acid or linolenic acid is abundant in the seed fat of one species, whilst in another related species a quite different unsaturated acid replaces these almost entirely. The most familiar examples of the latter are: (i) the prominence of elæostearic glycerides in the seeds of *Aleurites Fordii* and *montana*, whilst in other species of *Aleurites* polyethenoid unsaturation is confined to linoleic and linolenic glycerides; and (ii) the abundance of ricinoleic glycerides in the seeds of *Ricinus* species. Such cases are therefore classified separately, as a sub-group to I and II (above), according to the plant families concerned (Euphorbiaceæ, Rosaceæ, Cucurbitaceæ). The other type, in which specific saturated acids (other than palmitic) are a feature of the seed fats, are grouped primarily with reference to their specific saturated acids, irrespective of whether linoleic acid is also a major component. Similarly, the occurrence of specific unsaturated acids, such as erucic, petroselinic, chaulmoogric, and hydnocarpic, has been dealt with by separating into corresponding groups the seed fats in which they occur as major components of the mixed glycerides.

GENERAL CLASSIFICATION OF SEED FATS ACCORDING TO THEIR MAJOR COMPONENT ACIDS

Table	Major Component Acids	Botanical Families Represented
49	Linoleic, linolenic, (oleic)	Coniferæ; Juglandaceæ, Moraceæ, Celastraceæ, Labiatæ, Urticaceæ, Passifloraceæ, Valerianaceæ, Œnotheraceæ, Linaceæ, Rhamnaceæ, Elæagnaceæ.
50	Linoleic, oleic	Betulaceæ, Fagaceæ, Ulmaceæ, Olacaceæ, Amarantaceæ, Papaveraceæ, Typhaceæ, Capparidaceæ, Staphyleaceæ, Hippocastanaceæ, Vitaceæ, Theaceæ, Myrtaceæ, Oleaceæ, Asclepiadaceæ, Pedaliaceæ, Scrophulariaceæ, Plantaginaceæ, Dipsacaceæ, Compositæ.
51	Linoleic, oleic, or linolenic, or elæostearic, licanic; or ricinoleic.	Rosaceæ, Euphorbiaceæ, Cucurbitaceæ.
52	Palmitic, oleic, linoleic	Berberidaceæ, Menispermaceæ, Magnoliaceæ, Anonaceæ, Rutaceæ, Anacardiaceæ, Tiliaceæ, Malvaceæ, Bombacaceæ, Caryocaraceæ, Caricaceæ, Lecythidaceæ, Combretaceæ, Apocynaceæ, Solanaceæ, Martyniaceæ, Acanthaceæ, Rubiaceæ, Caprifoliaceæ.
53	„ „ „	Gramineæ.
54	Petroselinic, oleic, linoleic	Umbelliferæ, Araliaceæ.
	Acetylenic acids:	
	Tariric	Simarubaceæ (*Picramnia* sp.).
	Octadecen-ynoic	Olacaceæ (*Onguekoa* sp.).
55	Cyclic unsaturated acids (chaulmoogric, hydnocarpic, gorlic).	Flacourtiaceæ.
	Eicosenoic, (oleic, linoleic)	Olacaceæ (*Ximenia* sp.); Sapindaceæ; Buxaceæ (*Simmondsia* sp.).
56	Erucic, oleic, linoleic	Cruciferæ, Tropæolaceæ.
57	Oleic, linoleic, arachidic, lignoceric.	Leguminosæ, Moringaceæ, Ochnaceæ, Sapindaceæ.
58	Stearic, palmitic, oleic	Gnetaceæ; Meliaceæ, Sterculiaceæ, Guttiferæ, Dipterocarpaceæ, Burseraceæ, Sapotaceæ, Convolvulaceæ, Verbenaceæ.
59A	Lauric, myristic, (palmitic)	Lauraceæ, Myristicaceæ, Simarubaceæ, Vochysiaceæ, Salvadoraceæ.
59B	Lauric, myristic, (palmitic)	Palmæ.
59A	Capric, lauric.	Ulmaceæ.

SEED FATS WITH PALMITIC, OLEIC, LINOLEIC AND/OR LINOLENIC ACIDS AS MAJOR COMPONENTS

I AND II. SEED FATS IN WHICH LINOLEIC (WITH LINOLENIC AND/OR OLEIC) ACID PREDOMINATES

Major component acids: **LINOLEIC, LINOLENIC, OLEIC.**
Minor component acids: **Palmitic, (stearic).**

Tables 49 (pp. 156, 157) and 50 (pp. 158–160) give practically all the detailed figures which have been published for seed fats in which *linoleic*, *linolenic*, and *oleic* acids are the most important constituents. These groups, in spite of the small number of fatty acids concerned, were not easy to investigate until methods of analysis had been devised for the determination of oleic, linoleic, and linolenic acids in presence of each other. The ester-fractionation method does not help, of course, in this respect. Most of the figures quoted are based either upon analyses of the unsaturated acid fraction (obtained by a lead salt separation ("L"), or by low-temperature crystallisation ("C")), by means of the bromo-addition products (hexabromo- and tetrabromo-stearic acids) ("H"), or upon a combination of the Bertram oxidation process ("B") (for the total saturated acids) with the thiocyanogen method for estimating the three unsaturated acids ("T" or "K"). In some instances examination of bromo-addition products of unsaturated acids ("H") has been combined with fractionation of the esters of the saturated acids ("F"). In a few other cases the spectrographic determination ("S," p. 138) of linolenic and linoleic acid has been employed.

It should be appreciated that data obtained by the spectrographic method ("S") or with the aid of thiocyanogen values based on the empirically determined values for linoleic and linolenic acids ("T") are the more reliable. Those derived from the older form of calculation ("K") from thiocyanogen values give considerably less accurate figures for the proportions of the three unsaturated acids, whilst those based upon determinations of insoluble forms of tetra- or hexa-bromostearic acids almost certainly record considerably less than the amount of linoleic or linolenic acid actually present.

There is, perhaps, no very sharp line to be drawn, as regards component fatty acids, between the seed fats in Table 49 and those in Table 50, but it is convenient to subdivide them roughly into those in which linolenic acid is prominent and those in which it is not. It will be noticed that in both groups the fats are derived from the seeds of (i) large trees (conifers, beech, walnut, etc.), (ii) shrubs, and (iii) herbs of various families (e.g. Labiatæ, Compositæ, etc.).

The seeds of the larger trees of temperate climates apparently usually contain fatty oils of a "drying" nature. In both groups (Tables 49 and 50), the saturated acids usually amount to no more than about 10 per cent. of the whole, and consist mainly (generally to the extent of about 70 per cent.) of palmitic acid. Stearic acid is also present in most instances, but only to the extent of about 1–4 per cent. of the total acids.

The coniferous seeds shown in Table 49 sometimes contain fairly large amounts of linolenic acid, but in other cases this acid is absent or only present in small quantity; linoleic acid nearly always forms 50 per cent. or more of the total acids. The figures for the five *Pinus* species conform with the view that varieties indigenous to cool climates produce a more unsaturated type of seed fat, and *vice versa*.

In contrast to the coniferous gymnosperms in Table 49, it is interesting to find that the only seed fat yet examined from the relatively few tropical gymnosperms (*Gnetum scandens*, Table 58, p. 194) contains quite a different mixture of component acids (palmitic 14, stearic 56, oleic 27, linoleic 3 per cent.). It thus closely resembles certain families of tropical angiosperms, such as Sapotaceæ or Guttiferæ, in the general composition of its seed fatty acids, and especially in the high content of stearic acid.

Seeds of the walnut and beech families, according to the data here presented, are less unsaturated in general than those of conifers; indeed, hickory nut oil is practically of the " non-drying " olive type. It would be very interesting to have a much more complete set of data on the seed fats of the larger trees, and such a list is indeed essential before any adequate generalisation can be put forward; the vague general characteristics which have been given for seed oils of the ash, hazel, and a few other trees suggest that most of them are of the same simple type as those included in these tables, but that the state of unsaturation varies from predominantly oleic to high linoleic (and possibly linolenic) content in different cases.

One striking exception to the general observation that closely related botanical forms share similarities in their seed fat component acids is encountered amongst the seed fats of the larger trees, namely, that of species of the common elm. The seed fat of the American elm, *Ulmus americana*, studied in some detail by Schuette *et al.*[43] contains only about 11 per cent. of oleic and 9 per cent. of linoleic acid, whilst the saturated acids include over 60 per cent. of *n*-decanoic (capric) acid, with small proportions of octanoic, lauric, myristic and palmitic acids (*cf.* Table 59A, p. 200). Earlier but less detailed examinations of European elm seeds (*U. campestris*) by Pawlenko [44] and by Beythien *et al.*[45] indicate a similar composition, with capric acid as the predominating component. The elm thus seems to stand apart from all other trees or shrubs in the high content of capric acid in its seed fat; moreover, no other seed fat from plants common to temperate climates has yet been reported with acids of so saturated a character and with high proportions of lauric as well as capric acids. The elm family is grouped botanically in the Urticales with the families Urticaceæ and Moraceæ; such other seed fats of these three families as have been studied (hackberry, hempseed) are of the types common to those in Tables 49 and 50, the major component acids including linoleic, oleic, and linolenic, whilst the saturated acids are less prominent and are confined to palmitic and stearic acids.

The shrubs and herbs quoted in Tables 49 and 50 possess seed fats similar in general composition to those of the larger trees previously mentioned; those of some other plant families might also have been included except that, whilst many members of the latter contain only the usual acids—oleic, linoleic, linolenic, palmitic—other species give rise to specific acids of a less usual type. As already explained (p. 153), these families are here dealt with separately; but reference to Tables 51 (Rosaceæ, Euphorbiaceæ, and Cucurbitaceæ) and 57 (Leguminosæ) will emphasise that in these families also the major component acids are confined in many instances to oleic, linoleic, and sometimes linolenic, with palmitic acid as a characteristic minor component. Leaving these four families aside, however, no plant family falling in Tables 49 and 50 appears in any of the subsequent tables,

TABLE 49. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS*

Major component acids: All unsaturated C_{18} acids : LINOLEIC, LINOLENIC, (OLEIC).
Minor component acids: Small amounts of palmitic, less stearic, and occasionally traces of arachidic (?).

		Habitat	Component Fatty Acids per cent. (wt.) Palmitic	Stearic	Oleic	Linoleic	Linolenic	Method	Observers
GYMNOSPERMS									
CONIFERÆ (PINACEÆ)									
Pinus cembra	Cedar nut oil	W. Siberia	—	—	33–36	31–34	17–28	K	Ivanov and Resnikova.[1]
,, *excelsa*	Red pine seed	Europe, N. America	← 8·2 →		12	57	22	L, H	Eibner and Reitter.[2]
,, *monophylla*	Pine nut	Southern U.S.A.	← 8·8 →		64	27	—	L	Adams and Holmes.[3]
,, ,,	,, ,,		2·9 (*a*)	0·4	61·7	29·6	—	F	Gill.[4]
,, *picea*	Fir seed	Europe, N. America	0·7	—	42	49	8	L, H	Friedrichs.[5]
,, *pinea*	Pine seed	Mediterranean coast	5·4	0·6	48	46	—	L, H	Matthes and Rossié.[6]
,, *pumila*		Russia	← 5 →		12	76	7	B, T	Pigulevski and Ivanova.[7]
,, *sabiniana*	Digger pine seed	U.S.A.	← 7 →		48	45	—	T	Semb.[8]
,, *sylvestris*	Pine seed	Europe, Asia, N. America	2·8	0·1	35	54·5	7·5	L, H	Friedrichs.[5]
,, ,,	,, ,,	,, ,,	4·1	3·1	9·5	58	25	L, H	Eibner and Reitter.[2]
Abies balsamea		U.S.A.	← 2 →		35	61	2	B, T	Benson and Calderwood.[9]
CONIFERÆ (TAXACEÆ)									
Torreya nucifera	Kaya oil	Japan	← 9 →		19	72	—	L, H	Ueno.[10]
ANGIOSPERMS									
JUGLANDACEÆ									
Carya cordifornia	Hickory nut	U.S.A.	6·5	5·5	88	—	—	L, H	Riebsomer *et al.*[38]
Hicoria pecan	,, ,,	,,	← 4 →		80	16	—	L, H	Boone.[11]
,, ,,	,, ,,	,,	3·3	1·9	78·7	16·1	—	F	Jamieson and Gertler.[12]
,, ,,	Pecan nut	,,	← 4 →		71	25	—	B, T	Bickford *et al.*[44]
Juglans regia	Walnut seed	Europe, Asia, N. America	4·6	0·9	18	73	3	F, H	Jamieson and McKinney.[13]
,, ,,	,, ,,	,, ,,	5·1	2·5	29	48	16	B, H	Wick.[14]
,, ,,	,, ,,	,, ,,	3·5 (*b*)	1·9	35	57	3	F, T	Jamieson and McKinney.[15]
,, ,,	,, ,,	,, ,,	← 9 →		18	63	10	B, K	Ivanov and Berdichevski.[16]
,, ,,	,, ,,	Japan	← 10·8 →		9	76	4	L, T	Ueno and Nishikawa.[17]
,, ,,	,, ,,		7·0	1·1	16	72	4	F, T	Griffiths and Hilditch.[18]
,, *manshurica*	,, ,,	Manchuria	2·9	0·6	19	76	2	L, H	Branke and Komissartschuk.[19]
,, *Sieboldiana*	,, ,,	Japan	← 6·6 →		20	67	6	B, T	Ueno and Nishikawa.[17]
MORACEÆ									
Cannabis sativa	Hemp seed	Temperate zones	← 10·1 →		16	46	28	B, T	Kaufmann and Juschkewitsch.[20]
,, ,,	,, ,,	,, ,,	← 4·5 →		14	65	16		Schestakow and Kuptschinsky.[21]
,, ,,	,, ,,	,, ,,	5·8	1·7 (*c*)	6	70	15	F, T	Griffiths and Hilditch.[18]
Treculia africana	Bread fruit	Sierra Leone	24·1	11·7	45·7	18·5	—	F	Ichaporia.[22]
CELASTRACEÆ									
Celastrus scandens	Bittersweet vine	U.S.A.	12·1	2·7	1	45	39	L, T	Barkenbus and Krewson.[23]
,, *paniculatus*		India	22·3	4·3	22	35	16	F, T	Gunde and Hilditch.[24]
LABIATÆ									
Lallemantia iberica	Lallemantia	Russia	← 13 →		8	22	57	B, K	Lesyuis [39]
,, ,,	,,	S. W. Russia	← 9 →		1	36	53	B, K	Steger and van Loon.[46a]
,, *royleana*	,,	India	10·2	3·3	60·1	26·4	—	L	Malavya and Dutt.[40]
Ocimum basilicum	Sweet Basil seed	India	7·0	0·2	11	60	21	F, H	Patwardhan.[25]
,, *kilimandscharicum*		Sudan	← 8 →		17	14	61	L, T	Henry and Grindley [41]
Perilla ocimoides	Perilla seed	Japan, East Indies	← 6·7 →		23	—	70	B, T	Kaufmann.[26]
,, ,,	,, ,,	,,	← 7·6 →		14	16	63	B, T	Kaufmann.[26]
Salvia hispanica	Chia seed	Mexico	5·3	2·9	12	32·5	47	F, H	Baughman and Jamieson.[27]
,, ,,	,, ,,	Holland	← 10 →		—	32	58	B, K	Steger and van Loon.[46b]
URTICACEÆ									
Urtica dioica	Stinging nettle	Europe	← 7 →		12	79	2	B, K	Prögler [42]
PASSIFLORACEÆ									
Passiflora edulis	Passion fruit	U.S.A.	7·3	1·9 (*d*)	17	73	—	F, T	Jamieson and McKinney.[28]
VALERIANACEÆ									
Valerianella olitorea	Corn salad	Europe	← 12·4 →		18	61	9	B, T	Steger and van Loon.[29]
ŒNOTHERACEÆ									
Œnothera biennis	Evening primrose seed	Temperate zones	5·6	—	27	65	2	L, H	Heiduschka and Luft.[30]
			5·7	—	26	58	10*	L, H	Eibner and Schild.[31]
LINACEÆ									
†*Linum usitatissimum*	Linseed	Widely distributed							
,, ,,	,,	Calcutta	← 8·9 →		19	23	49	L, H	Eibner and Brosel.[32]
,, ,,	,,	La Plata	← 10·8 →		27	1	61	B, T	Gay.[33]
,, ,,	,,	,,	← 10·3 →		21	15	53	B, T	Gay.[33]
,, ,,	,,	,,	← 10·7 →		18	18	53	B, T	Gay.[33]
,, ,,	,,	,,	← 9·0 →		16	31	44	L, T	Kaufmann and Keller.[34]
,, ,,	,,	,,	← 11·3 →		14	29	45	L, T	Kaufmann and Keller.[34]
,, ,,	,,	,,	5·4	3·5 (*e*)	19	24	47	F, T	Griffiths, Hilditch and Jones.[35]
,, ,,	,,		← 8 →		23	22	47	T	Mitchell *et al.*[43]
,, ,,	,,		← 6 →		29	18	47	S	Mitchell *et al.*[43]
,, ,,	,,		7	8 (*f*)	13	17	54	C, F, S	Gunstone and Hilditch.[45]
RHAMNACEÆ									
Rhamnus cathartica	Buckthorn seed	Temperate zones	1·2	6·3	31	37	24	L, H	Krassowski.[36]
ELÆAGNACEÆ									
Hippophaë rhamnoides	Seeds of sea buckthorn	Siberia	← 10·9 →		41	33	15		Ruchkin.[37]

(*a*) Also 5·4 per cent. myristic acid.
(*b*) Also 0·5 per cent. myristic acid.
(*c*) Also 1·1 per cent. arachidic acid.
(*c′*) Also 0·1 per cent. myristic and 0.3 per cent. arachidic acids.
(*d*) Also 0·3 per cent. arachidic acid.
(*e*) Also 0·2 per cent. myristic and 0·6 per cent. arachidic acids.
(*f*) Also 1 per cent. arachidic acid.

* $\Delta^{6,9,12}$-linolenic acid in *Œnothera* oil.
† See also text for further data, p. 163.

TABLE 50. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS*

Major component acids: All unsaturated C_{18} acids—LINOLEIC and/or OLEIC.
Minor component acids: Small amounts of palmitic and less stearic, (linolenic, myristic, arachidic).

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.) PALMITIC	STEARIC	OLEIC	LINOLEIC	LINOLENIC	METHOD	OBSERVERS
BETULACEÆ									
Corylus avellana	Hazelnut, filbert	Italy	3·2 (*a*)	1·7	91	4	—	F, T	Schuette and Chang.[1]
,, ,,	,, ,,	France	← 8·4 →		82	10	—	B, H	Bertram.[2]
FAGACEÆ									
Fagus sylvatica	Beech nut	Temperate zones	5·2	3·7	81	10	Trace	L, H	Heiduschka and Roser.[3]
,, ,,	,, ,,	,,	← 12·0 →		48	38	2	B, T	Delvaux.[4]
Quercus palustris	Pin, swamp oak (acorn)	U.S.A.	← 16 →		55	29	—	B, T	Hutchins and Simpson.[5]
,, *incana*	Indian oak (acorn)	India	17·1	— (*b*)	82·0	—	—	F	Puntambekar and Krishna.[6]
ULMACEÆ (see text, pp. 155, 200).									
Celtis occidentalis	Hackberry seed	U.S.A.	—	5·3	16	78	—	L	Schuette and Zehnpfennig.[7]
OLACACEÆ									
Agonandra brasiliensis	Ivory wood seed	Argentine	1·4 (*x*)	—	12	37	— (*c*)	F	Gurgel and de Amorim.[8]
Coula edulis	Coula seed	Tropical Africa	← 1·7 →		95	3	—	B, K	Steger and van Loon.[9]
Ximenia americana		India	—	1·2 (*d*)	60·8	6·7	—	F	Puntambekar and Krishna.[10]
,, ,,	Lumeque seed	W. Africa	—	4 (*r*)	54	10 (*r*)	—	F	Boekenoogen.[11]
Onguekoa Gore Engler syn. *Ongokea Klaineana* Pierre	Isano nut	Congo	(see text, p. 161)						Steger and van Loon, Boekenoogen, Castille.[12]
AMARANTACEÆ									
Amaranthus retroflexus	Pigweed	Oregon, U.S.A.	18·9	1·9	51·3	27·9	—	F	Christensen and Miller.[13]
TYPHACEÆ									
Typha latifolia	Reed-mace, Cat-tail	U.S.A.	← 23 →		17	60	—	L	Schuette and Gagneron.[64]
,, ,,		,,	← 12·5 →		15	72·5	—	T	Clopton and von Korff.[70]
PAPAVERACEÆ									
Argemone mexicana	Argemone seed	Tropics	8·0	6·0 (*f*)	21·8	48·0	0·6	F, H	Iyer, Sudborough and Ayyar.[15]
,, ,,	,, ,,	Mexico	11·8 (*s*)	1·9	22·7	62·3	—	F	Jamieson and Rose.[14]
Papaver somniferum	Poppy seed	Temperate and sub-tropics	4·8	2·9	30·1	62·2	—	L, H	Eibner and Wibelitz.[16]
,, ,,	,, ,,	Russia	← 10 →		25	65	—	B, K	Juchnovski.[17]
CAPPARIDACEÆ									
Capparis spinosa		,,	← 7–9 →		42–46	51–45	—	L	Zabrami *et al.*[53]
STAPHYLEACEÆ									
Staphylea pinnata		Mid-Europe	3·4	—	91	5	0·5	L	Ferencz and Cseresznyés.[18]
,, ,,		,, ,,	4	—	56	40	—	B	Pavlov.[19]
HIPPOCASTANACEÆ									
Æsculus hippocastanum	Horse chestnut	Temperate zones	4·4	3·6	66	25	1	F, T	Kaufmann and Baltes.[20]
VITACEÆ									
Vitis riparia	Wild grape seed	Temperate zones	3·4	1·9	44	50	—	L, H	Beal and Beebe.[21]
,, *rotundifolia*	Muscadine grape seed	Southern U.S.A.	← 15 →		20	65	—	T	Pickett.[54]
,, *vinifera*	Grape seed	Sub-tropics	5·5	2·4	37	55	—	L	Rabak.[22]
,, ,,	,, ,,	,, ,,	5	10	20 (*g*)	50	—		Carrière and Brunet.[23]
,, ,,	,, ,,	Bessarabia	6·5	2·3	33 (*h*)	46	Trace	L, H	Otin and Dima.[24]
,, ,,	,, ,,	California	6·5	2·9 (*i*)	31	60	—	F, T	Jamieson and McKinney.[25]
,, ,,	,, ,,	S. Germany	← 12 →		17	71	—	B, K	Kaufmann and Fiedler.[26]
,, ,,	,, ,	Pfalz, Germany	← 12–16 →		23–15	65–69	—	B, K	Kaufmann and Sprick.[27]
,, ,,	,, ,,	Swiss	← 14·5 →		27	58·5	—	T	Viollier and Iselin.[69]
THEACEÆ									
Thea sinensis	Tea seed	China, India, etc.	7·6 (*j*)	0·8	83·3	7·4	—	F	Griffiths and Hilditch.[28]
,, ,,	Chinese tea seed	China	← 6 →		84	10	—	L	Ueno and Ueda.[29]
Camellia japonica	Japanese tea seed	Japan	← 11 →		87	2	—	B, K	Kaufmann and Baltes.[30]
,, *sasanqua*	Ceylon tea seed	Ceylon	← 13 →		72	15	—	T	Child.[60]
MYRTACEÆ									
Psidium guyova	Guyova seed	India	← 16 →		56	28	—	B, T	Varma, Godbole, and Srivastava.[31]
OLEACEÆ									
Olea europæa	Olive kernel	Portugal	6	4	83	7	—	L	Klein.[32]
ASCLEPIADACEÆ									
Asclepias cornuti		Russia	← 11 →		35	54	—	B	Matzurevitsch.[33]
,, *syriaca*	Milkweed	U.S.A.	← 3 →		50	47	—	B, T	Lanson *et al.*[65]
PEDALIACEÆ									
Sesamum indicum	Sesame seed	India	7·8	4·7 (*k*)	49·4	37·7	—	F, H	Jamieson and Baughman.[34]
,, ,,	,, ,,	Siberia	← 16 →		37	47	—	B	Rudakov and Belopolski.[35]
,, ,,	,, ,,	India	9·1	4·3 (*l*)	45·4	40·4	—	F	Hilditch, Ichaporia, and Jasperson.[36]
,, ,,	,, ,,	,,	8·2	3·6 (*a′*)	45·3	41·2	—	C, F, S	Hilditch and Riley.[38]
SCROPHULARIACEÆ									
Verbascum thapsus	Mullein seed	Bohemia	← 6 →		28	57	8	B, K	Votocek, Valentin and Bulir.[37]
PLANTAGINACEÆ									
Plantago ovata	Isabghol	India	4·2	7·7 (*m*)	38·0	49·2	Trace	L, F	Pendse and Dutt.[39]
DIPSACACEÆ									
Dipsacus fullamum	Teazlewort	Russia	← 4 →		53	43	—	B	Ivanov.[40]

TABLE 50. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS—continued*

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.)					METHOD	OBSERVERS
			PALMITIC	STEARIC	OLEIC	LINOLEIC	LINOLENIC		
COMPOSITÆ									
Ambrosia elator	Ragweed	U.S.A.	5·5	4·8	19·9	69·8	—	T	Roedel and Thornton.[55]
Carthamus tinctorius	Safflower seed	Asia	6	4	38	51	1	L	Zukervanik.[41]
,, ,,	,, ,,	,,	← 19 →		24	57	—	B, K	Juchnovski.[15]
,, ,,	,, ,,	India	3 (*t*)	1	33	61	—	F	Vidyarthi.[56]
,, ,,	,, ,,	,,	2·1 (*u*)	2·0	37·6	56·7	—	F	Lagawankar *et al.*[61]
,, ,,	,, ,,	American	4·2	1·6 (*n*)	26·3	67·4	0·1	F, H	Jamieson and Gertler.[42]
,, ,,	,, ,,	,,	← 9 →		13	78	—	B, T	van Loon.[43]
,, ,,	,, ,,	New Mexico	← 7 →		19	71	3	B, T	Bickford *et al.*[63]
,, ,,	,, ,,	Germany	← 8 →		13	78	1	B, T	Kaufmann and Fiedler.[44]
Cichorium intybus	Chicory seed	India	← 22 →		33	45	—	L	Misra and Dutt.[45]
Cnicus benedictus	Thistle seed		2·4	1·6	71	25	—	L	Ferencz.[46]
Cynara cardunculus	Argentine thistle	S. America	← 12 →		22	64	2	?	Eckstein.[57]
Guizotia abysinica	Niger seed	India	8·2 (*o*)	4·8	30·3	52·9	—	F	Sahasrabuddhe and Kale.[47]
,, ,,	,, ,,	,,	7·0 (*v*)	3·2	15·1	71·1	—	F	Hilditch and Sime.[58]
,, ,,	,, ,,	,,	← 12 →		16	72	—	S	Hilditch, Morton and Riley.[68]
,, ,,	,, ,,	,,	← 10 →		16	72	2	T	Pye.[66]
Helianthus annuus	Sunflower seed	America	3·5	2·9 (*p*)	34·1	58·5	—	F, H	Baughman and Jamieson.[48]
,, ,,	,, ,,	Congo	3·7	1·6 (*q*)	42·0	52·0	—	F	Pieraerts.[49]
,, ,,	,, ,,	Russia	← 10 →		36	54	—	L, H	Eibner.[50]
,, ,,	,, ,,	,,	← 5 →		33	62	—	B, K	Juchnovski.[17]
,, ,,	,, ,,	,,	← 10 →		33	57	—	B, K	Rankoff.[51]
,, ,,	,, ,,	,,	5·6	2·2 (*w*)	25·1	66·2	—	F	Hilditch. and Zaky[62]
Vernonia anthelmintica		India	7 (*y*)	6	6	10	—	F	Vidyarthi.[67]
Xanthium strumarium	Cockle burr seed	Russia	1·5	7·0	27	65	—	L, H	Branke and Gutt.[52]
,, ,,	,, ,, ,,	,,	← 8·3 →		27·5	64·2	—	L	Maximov.[59]

(*a*) Also 0·2 per cent. myristic acid.
(*b*) Also 0·9 per cent. lignoceric acid.
(*c*) Also 47 per cent. ricinoleic acid.
(*d*) Also 15·2 per cent. cerotic acid, 14·6 per cent. ximenic acid, $C_{26}H_{50}O_2$, and 1·5 per cent. resin acids.
(*e*) Also 0·2 per cent. arachidic acid.
(*f*) Also 5·8 per cent. hexadecenoic and 9·8 per cent. ricinoleic acids.
(*g*) Also 10 per cent. ricinoleic and 5 per cent. erucic acids.
(*h*) Also 12·5 per cent. hydroxy-acids recorded.
(*i*) Also 0·1 per cent. arachidic acid.
(*j*) Also 0·3 per cent. myristic and 0·6 per cent. arachidic acids.
(*k*) Also 0·4 per cent. arachidic acid.
(*l*) Also 0·8 per cent. arachidic acid.
(*m*) Also 0·9 per cent. lignoceric acid.
(*n*) Also 0·4 per cent. arachidic acid.
(*o*) Also 3·3 per cent. myristic+lauric, and 0·5 per cent. arachidic acids.
(*p*) Also 0·6 per cent. arachidic and 0·4 per cent. lignoceric acids.
(*q*) Also 0·7 per cent. arachidic acid.
(*r*) Also 2 per cent. cerotic, 25 per cent. ximenic ($C_{26}H_{50}O_2$), and 5 per cent. lumequic ($C_{30}H_{58}O_2$) acids.
(*s*) Also 0·3 per cent. myristic, 0·1 per cent. lignoceric, and 0·9 per cent. hexadecenoic acids.
(*t*) Also 1·5 per cent. myristic and 0·5 per cent. arachidic acids.
(*u*) Also 0·4 per cent. myristic and 1·2 per cent. arachidic acids.
(*v*) Also 1·1 per cent. myristic, 0·6 per cent. arachidic, and 1·9 per cent. hexadecenoic acids.
(*w*) Also 0·9 per cent. arachidic acid.
(*x*) Also 2·3 per cent. myristic acid.
(*y*) Also 7 per cent. myristic, 2 per cent. resin acids, and 62 per cent. *vernolic* (probably 11-hydroxy-Δ^9-octadecenoic) acid.
(*z*) Also 1 per cent. arachidic and traces of myristic and hexadecenoic acids.
(*a′*) Also traces of myristic, 1·1 per cent. arachidic, and 0·5 per cent. hexadecenoic acids.

in which the major component acids of the seed fats are different. In other words, a specific relationship between seed fat component acids and botanical grouping commences to appear even in the case of the relatively simple and common mixtures of fatty acids recorded in Tables 49 and 50, a relationship which becomes still more distinct as seed fats are considered in which other acids appear as major components in addition to, or substitution for, palmitic and the C_{18} unsaturated acids.

At the same time, one or two of the plant families included in these two tables appear to possess unusual features in their seed fats. Both species of *Celastrus* which have been examined have been observed to include in their seed fats, in addition to the usual higher fatty acids, appreciable proportions of formic, acetic and benzoic acids; the most recent work (Gunde and Hilditch, Table 49, *loc. cit.*) indicates, however, that the latter are present not as glycerides, but in combination with a complex water-soluble polyhydric and probably cyclic alcohol, the exact nature of which is as yet unknown. The naturally occurring lower acyl esters of this substance are evidently soluble in the seed fat and removed to some extent with the latter during its extraction from the seed.

The few examples of the Olacaceæ which have been studied suggest that seed fats in this family may be somewhat heterogeneous in composition.

Thus the seed fat of *Onguekoa Gore* Engler (syn. *Ongokea klaineana* Pierre) is most unusual in its chief component acid, which was believed by Steger and van Loon [54a] to be di-unsaturated, one double bond being ethylenic and the other acetylenic. These workers also mentioned the presence of an acid, m.p. 38–39°, containing one ethylenic and two acetylenic linkings, and Boekenoogen [54b] stated that this acid is the main component of the fat. Later, Steger and van Loon [54a] also agreed that the chief component acid (called by them "isanic" acid, $C_{18}H_{26}O_2$, m.p. 39·5°) is the one which contains one ethenoid (vinyl) and two acetylenic groups. Subsequent studies by Castille [54c] showed that the ethyl ester of this acid (which he termed "erythogenic" acid, m.p. 39·5°) yields on ozonisation 1 mol. each of formaldehyde, oxalic acid, adipic acid, and ethyl hydrogen azelate, so that the acid must be formulated either as

$$CH_2{:}CH.C{:}C.[CH_2]_4.C{:}C.[CH_2]_7.COOH,$$

or

$$CH_2{:}CH.[CH_2]_4.C{:}C.C{:}C.[CH_2]_7.COOH.$$

In addition to this peculiar main component acid, small proportions of oleic, linoleic and saturated acids, and possibly an unsaturated hydroxy-acid, are present in the fat.*

Coula seed fat is marked by extreme simplicity of composition and extremely high oleic acid content (95 per cent.); but ivory wood seed fat contains, in addition to linoleic and oleic acids, nearly 50 per cent. of ricinoleic (hydroxyoleic) acid, and in the remaining instance (*Ximenia americana* seed fat), in addition to large proportions of oleic acid, about 15 per cent. each of cerotic (*n*-hexacosanoic) acid, $C_{26}H_{52}O_2$, and of a corresponding mono-ethenoid *n*-hexacosenoic ("ximenic") acid, $C_{26}H_{50}O_2$, have been encountered.*

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* The seed fat of *Santalum album* (family Santalaceæ, which like Olacaceæ is placed in the group of Santalales) also appears to contain an unusual fatty acid. The component acids include 49 per cent. of "liquid" unsaturated acids and 51 per cent. of "solid" acids (Madhuranath and Manjunath [48]); the latter, except for a small amount of palmitic acid, consist chiefly of a solid triethenoid, non-conjugated acid, $C_{18}H_{30}O_2$, m.p. 41–42°, of undetermined constitution.

According to Boekenoogen,[105] *Ximenia americana* seed fat contains about 25 per cent. of " ximenic " (Δ^{17}-hexacosenoic) and about 5 per cent. of " lumequic " (Δ^{21}-tricosenoic) acids.

The data in Tables 49 and 50 (and also those of Tables 51 and 57) form suitable material for study of the connection between temperature of habitat and relative unsaturation of the seed fats. The only conclusion which emerges is that no wide generalisation on this point is permissible. The studies of Ivanow[47] and others have demonstrated clearly that a given plant species, capable of existence in different climates, produces when grown in a cold climate more unsaturated (linoleic and linolenic) acids in its seed fat than when it is grown in a warmer climate. To argue in addition, as has been attempted, that tropical plants tend to produce more saturated kinds of seed fats than those of cooler habitat appears to the writer to be far too sweeping and, moreover, is not by any means substantiated by the facts. It is, of course, obvious that seeds in whose fats the higher saturated acids predominate will be those of tropical or sub-tropical growth, since the seed fats must be fluid at the temperature of the living plant. Let us, however, consider the case of species with varying proportions of the different unsaturated acids, the mixed glycerides of which are liquid at the ordinary temperature of the temperate or even sub-arctic regions.

Cases for relation between temperature of growth and component unsaturated acids in the seed fats could be made out, in addition to the *Pinus* species already referred to (p. 155), for members of the Moraceæ and Celastraceæ listed in Table 49. In the former case, the West African *Treculia africana* seed fat is much less unsaturated in composition than hempseed, which grows in temperate climates ; in the other case, the seed fat of the North American *Celastrus scandens* obviously contains much more linoleic and linolenic acids, and less oleic and saturated acids, than the sister species, *C. paniculatus*, from India. Similarly, in the data (Table 50) for species of oak (Fagaceæ), of the Papaveraceæ, of sesame (Pedaliaceæ), of safflower (Compositæ) and possibly of the grape (Vitaceæ), and again in Spanish or Virginian as contrasted with West African groundnut oil (Leguminosæ, Table 57), there is some evidence for greater proportions of the more unsaturated acids in the respective plants which inhabit cooler, as compared with those from warmer, regions.

On the contrary, however, seed fats of numerous tropical or sub-tropical plants are as highly unsaturated as any of temperate climatic origin in such cases as those of sweet basil, perilla, chia, or safflower seeds ; whilst the Calcutta linseed oil quoted is recorded as containing nearly 50 per cent. of linolenic acid, a figure which is nearly as high as any given in Table 49 for Argentine linseed oils. Among the Rosaceæ and Euphorbiaceæ species (Table 51, pp. 166, 167) the absence of any general correlation between degree of general unsaturation and climatic temperature becomes absolutely clear. In the rose family, the species common to temperate regions—*Prunus* species, hawthorn, blackberry—usually contain much oleic and linoleic acids in their seed fats, with occasionally some linolenic acid in addition ; but certain tropical species, namely, *Licania rigida* and *Parinarium* species, are characterised by the presence in their seed fats of large amounts of conjugated triethenoid and, in one instance, *tetraethenoid* acids of the C_{18} series. Similarly, in the Euphorbiaceæ, whilst the caper spurge appears to contain over 90 per cent. of oleic acid in its seed fat, tropical species such as those of

Hevea and *Aleurites* are uniformly characterised by high proportions of highly unsaturated acids, notably in the case of the conjugated triethenoid elæostearic acid.

Of the more common oils mentioned in Tables 49 and 50, those of walnut, hemp, perilla, chia, linseed, argemone, and poppy are usually classed as " drying " oils ; soya bean and safflower oils are sometimes referred to the " drying," and sometimes to the " semi-drying " type ; sesame, sunflower, and grape seed oils are definitely " semi-drying " oils, and almond, groundnut, and olive are " non-drying." If we try to correlate the component fatty acids of an oil with the conventional classification as to drying properties, we may say that in " non-drying " oils linoleic acid does not form much more than 20 per cent. of the mixed fatty acids ; but the boundary between " semi-drying " and " drying " oils is less easy to define. The presence of 5 per cent. or more of linolenic acid, especially when at least 50 per cent. of linoleic acid is also present, confers definite " drying " properties, and naturally the combination of relatively large amounts of linolenic acid with as little as about 20 per cent. of linoleic acid leads to the same result. On the other hand, when linoleic acid exceeds 55–60 per cent. of the mixed acids, an oil is often referred to the " drying " class, although linolenic acid may be absent or only present in very minor amounts ; but a content of less than about 55 per cent. of linoleic, combined with absence of linolenic, acid seems to connote a " semi-drying " oil. Thus the component acids apparently requisite for a good " drying " oil are either (i) a minimum of about 55 per cent. of linoleic acid with, at least, traces of linolenic acid, or (ii) substantial proportions of linolenic acid with, on occasion, correspondingly reduced amounts of linoleic acid.

Linseed oils. In addition to the typical data given in Table 49 (p. 157), analyses of many varieties of linseed oil have been published in recent years and, in view of the technical importance of this oil, ought to be mentioned here.

Thus in 1939 Woodward [106] published data for specimens of four main types of linseed oil, analysed by the lead salt separation ("L"), Bertram oxidation ("B"), and thiocyanogen ("T") methods. His figures for the proportions of saturated ("Satd."), oleic ("Ol"), linoleic ("Lin") and linolenic ("Len") in the mixed fatty acids were:

VARIETY	SATD.	OL.	LIN.	LEN.
Indigene	11	13	15	61
Baltic	7	20	16	57
Calcutta	9	24	14	53
La Plata	10	26	12	52

In 1939, also, Rose and Jamieson [107] gave data for three varieties of linseed grown in different parts of the United States, based on analyses by the ester-fractionation ("F") and thiocyanogen ("T") methods. Their results were as follows (including the individual proportions of palmitic ("P") and stearic ("S") acids):

VARIETY	GROWN IN	OIL I.V.	P	S	OL.	LIN.	LEN.
Bison	N. Dakota (south)	144·1	6·7	4·7	36	21	30
,,	,, (north)	160·7	6·3	4·2	29	22	38
,,	,, ,,	179·8	6·3	2·5	19	24	47
,,	Texas	174·0	4·6	3·5	25	24	42
Punjab	,,	168·1	4·1	5·0	28	20	43
,,	California	184·9	5·2	5·1	22	10	58
Abyssinian	,,	197·3	7·2	2·3	16	10	64

In 1943, Painter and Nesbitt,[108] by means of the Bertram oxidation ("B") and thiocyanogen ("T") procedures, made analyses of a very large number of linseed oils from flax seed grown in various parts throughout the United States and Canada. Samples with a range in iodine values of from 128 to 203 were collected. The authors say " Adverse climatic conditions, high temperature, and insufficient moisture while the seed ripens sometimes produce linseed oils with low iodine values. These conditions were not uncommon in 1936. Occasionally, low iodine value oils have been produced in the Northwest Great Plains in other years." These workers conclude further from their results that each variety has its own characteristics as regards the composition of the oils produced in the seeds, but that the composition is always affected by the location and conditions of growth. Oils from each variety produced in Nebraska had most oleic and least linolenic acid, whilst those from seed grown in Nova Scotia had most linolenic and least oleic acid. A selection from the data of Painter and Nesbitt is appended.

Variety	Grown in	Oil	Component Fatty Acids			
		I.V.	Sat.	Ol.	Lin.	Len.
Bison	Nebraska	155·4	12	32	21	35
,,	Minnesota	162·8	11	30	18	40
,,	N. Dakota	164·7	10	34	12	44
,,	S. Dakota	171·5	10	27	19	44
,,	Montana	177·0	10	25	18	47
,,	Oregon	182·4	9	22	20	49
,,	Saskatchewan	187·0	9	22	15	54
,,	Nova Scotia	196·0	9	16	16	59
Redwing	Nebraska	171·6	10	25	22	43
,,	Minnesota	181·8	10	23	15	52
,,	N. Dakota	178·2	9	25	17	49
,,	S. Dakota	180·5	10	23	17	50
,,	Montana	187·6	9	19	20	52
,,	Oregon	196·5	9	17	14	60
,,	Saskatchewan	195·1	8	16	18	57
,,	Nova Scotia	201·7	9	12	18	61
Linota	Nebraska	170·6	9	26	25	40
,,	Minnesota	179·0	9	25	18	48
,,	N. Dakota	176·9	9	26	18	47
,,	S. Dakota	181·6	9	19	27	45
,,	Montana	188·2	8	21	18	53
,,	Oregon	190·4	8	21	16	55
,,	Saskatchewan	196·6	7	18	16	59
,,	Nova Scotia	202·8	7	14	17	62
Rio	Nebraska	155·8	14	31	15	40
,,	Minnesota	161·6	14	29	13	44
,,	N. Dakota	162·9	14	28	14	44
,,	S. Dakota	172·4	13	21	21	45
,,	Montana	177·8	12	25	10	53
,,	Oregon	186·6	9	19	20	52
,,	Saskatchewan	189·4	10	16	20	54
,,	Nova Scotia	194·7	10	14	17	59
Unknown	Unknown	127·8	16	41	23	20
,,	,,	135·4	16	42	12	30
,,	,,	146·2	13	37	19	31
,,	,,	154·6	12	31	19	35
,,	,,	177·0	12	21	19	48
,,	,,	200·0	9	12	19	60

The foregoing data illustrate the variations in linseed component acids which may obtain, but do not show the underlying causes clearly. Rose and Jamieson's figures suggest that different varieties of seed grown in the same area may produce very similar linseed oils whilst the oil from the same seed grown in different locations may be quite different in composition. Undoubtedly, as Painter and Nesbitt point out, high temperatures are conducive to the formation of less unsaturated oils, but other factors, such as soil, moisture, etc., clearly operate and the subject is evidently by no means a simple one.

For practical purposes, of course, it is evident that conditions of growth must be selected to give the best drying linseed oils. These will have iodine values of not less than 170–175, and their component acids will include 45 per cent. or more of linolenic acid ; the linoleic acid content of a good linseed oil may apparently lie between about 25 and 15 per cent., and the oleic acid content between about 20 and 30 per cent. There does not seem at present to be any well-defined information as to whether the linseed oils with exceptionally high linolenic acid contents (e.g. 60 per cent. linolenic, 15–20 per cent. linoleic, and 12–15 per cent. oleic acid) are significantly better for use in paints, etc., than the more usual type which contains 45–50 per cent. of linolenic acid.

IA. Seed Fats of the Families Rosaceæ, Euphorbiaceæ, Cucurbitaceæ

Major component acids: LINOLEIC, OLEIC, with LINOLENIC or a conjugated polyethenoid acid (ELÆOSTEARIC, LICANIC, etc.).
Minor component acids: Palmitic, (stearic), (oleic, linoleic).

Until comparatively recently it seemed as though the Euphorbiaceæ family was somewhat exceptional in possessing a few species which elaborated unusual acids in the seed fats—on the one hand ricinoleic (hydroxy-oleic) acid in *Ricinus* species, and on the other hand α-elæostearic ($\Delta^{9,11,13}$-octadecatrienoic) acid in two species of *Aleurites*. Within the last few years this peculiarity has not only been emphasised by the discovery that other species of this family (*A. trisperma* and *Ricinodendron africanum*) also contain α-elæostearic glycerides in their seeds, but the occurrence of the latter acid in quantity in the seed fats of several tropical species of plants belonging to the rose and the cucumber families has been recorded, whilst in addition isomeric forms of elæostearic acid, α-keto-elæostearic (licanic, couepic), and the conjugated tetraethenoid parinaric acid have also been observed in other seed fats of the two latter families. Therefore, since many other species in these three families confine polyethenoid unsaturation in their seed fats to the common forms of linoleic and linolenic glycerides, it is well to consider the three plant families together.

The data available at present are given in Table 51. Some of the recent observations on the more novel unsaturated acids are not on a quantitative basis, but are included in Table 51 in order to indicate the occurrence of the uncommon unsaturated components in question. It remains to be seen, of course, whether further research may not reveal the occurrence of these, or other, less common unsaturated acids in the seed fats of other botanical groups.

TABLE 51. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS OF THE FAMILIES ROSACEÆ, EUPHORBIACEÆ, AND CUCURBITACEÆ*

Major component acids: OLEIC, LINOLEIC (sometimes LINOLENIC, ELÆOSTEARIC or other conjugated polyene acid, RICINOLEIC).
Minor component acids: Palmitic and Stearic.

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.)				OTHER UNSATURATED COMPONENTS	METHOD	OBSERVERS
			PALMITIC	STEARIC	OLEIC	LINOLEIC			
ROSACEÆ									
Cratægus oxyacantha	Hawthorn seed	Temperate	2	1	81	11	5 per cent. linolenic	L, H	Vasterling.[1]
Cydonia vulgaris	Quince seed	Sub-tropics	← 9 →		43	47	1 per cent. linolenic	B, T	Steger and van Loon.[2]
Licania arborea	Cacahuananche nut	Mexico	← 12 →		5	8	ca. 73 per cent. α-licanic	Carbonyl, "Diene," B, K, etc.	Rose and Jamieson.[53]
,, *crassifolia*		E. Indies	← 8 →		5	22	ca. 65 per cent. α-licanic	"Diene," K	Sesseler and Rowaan.[54]
,, *rigida*	Oiticica nut	Brazil	8	4	?	?	88 per cent. highly unsaturated		van Loon and Steger.[3]
,, ,,	,, ,,	,,	← 10 →		← 16 →		74 per cent. α-licanic *		Kaufmann and Baltes.[4]
,, ,,	,, ,,	,,	?	?	?	?	α-licanic and α-elæostearic		Kappelmeier.[5]
,, ,,	,, ,,	,,	← 10 →		← 16 † →		α-licanic and α-elæostearic		Morrell and Davis.[6]
,, ,,	,, ,,	,,	← 11 →		6	—	78 per cent. α-licanic	B, K	McKinney and Jamieson.[7]
,, ,,	,, ,,	,,	6	5	4	—	82 per cent. α-licanic ; 3 per cent. hydroxy-acids.		Machado.[8]
Parinarium campestre	Behurada seed	E. Indies	← 15 →		27	9	49 per cent. α-elæostearic	"Diene," etc.	Steger and van Loon.[72a]
,, *corymbosum*	Taritih seed	,,	4	7	8	6	13 per cent. α-elæostearic and 62 per cent. α-licanic.	"Diene," etc.	Frahm.[55]
,, ,,	,, ,,	Java	← 12 →		← 10 →		15 per cent. α-elæostearic and 63 per cent. α-licanic.	"Diene," etc.	Steger and van Loon.[72b]
,, *glaberrimum*		E. Indies	3	4	some	some	ca. 70 per cent. α-licanic and some α-elæostearic.	"Diene," etc.	Frahm.[55]
,, *laurinum*	"Akarittom" seed	Pacific Is.	?	?	?	?	"Parinaric," i.e. $\Delta^{9, 11, 13, 15}$-octadecatetraenoic.		Tsujimoto and Koyanagi.[9]
,, ,,	,, ,,	,,	?	?	?	?			Farmer and Sunderland.[10]
,, *macrophyllum*	Neou seed	Sierra Leone	← 11 →		23	34	32 per cent. α-elæostearic		Steger and van Loon.[11]
,, ,,	,, ,,	Nigeria	12	2	40	15	31 per cent. α-elæostearic	C, F, S	Hilditch and Riley.[12]
,, ,,	,, ,,	W. Africa	← 12 →		21	37	30 per cent. α-elæostearic	?	Ivanow.[77]
,, *sherbroense*	Po-Yoak seed	Sierra Leone	← ca. 12 →		ca. 9–10	—	ca. 48 per cent. α-licanic and ca. 32 per cent. α-elæostearic.		Steger and van Loon.[13]
Prinsepia utilis		India	15·2 (*o*)	4·5	32·6	43·6	—	F	Puntambekar.[56]
Prunus amygdalus	Almond kernel	Temperate	← 3 →		77	20	—	L, H	Heiduschka and Wiesemann.[14]
,, ,,	,, ,,	,,	4·5(*a*)	—	77·0	17·3	—	F	Thompson.[15]
,, *armeniaca*	Apricot kernel	,,	2·6	1·2	64·4	31·8	—	F	Jamieson and McKinney.[16]
,, ,,	,, ,,	Mongolia	← 8 →		60	32	—		Tutiya.[57]
,, *cerasus*	Cherry kernel	Temperate	4·3(*b*)	2·9	49·5	42·3	—	F	Jamieson and Gertler.[17]
,, *domestica*	Plum kernel	,,	← 7 →		69	24	—	B, T	Delvaux.[18]
,, *laurocerasus*	Cherry laurel kernel	Sub-tropics	9·9(*c*)	1·7	73·4	13·2	—	F	(Miss) E. E. Jones.[19]
,, *lusitanica*	Portuguese ,, ,,	,,	6·6(*d*)	2·2	57·9	32·0	—	F	,, ,, [19]
Rosa canina	Wild rose	Russia	← 5 →		26	55	14 per cent. linolenic	B, T	Rusch and Ivanova.[58]
,, ,,	,, ,,	Holland	← 5 →		9	54	32 per cent. linolenic	B, K	Steger and van Loon.[72c]
Rubus cæsius	Blackberry seed	Temperate	5	—	16	76	3 per cent. linolenic	L	Krzizan.[20]

EUPHORBIACEÆ									
Aleurites cordata	Japanese tung seed	Japan	← 7 →		19	—	74 per cent. α-elæostearic	B, K	McKinney and Jamieson.[21]
,, *Fordii, montana*	Chinese ,, ,,	China, E. Indies	4·1	1·3	15	—	80 per cent. ,,	B, I.V.	Steger and van Loon.[22]
,, ,, ,,	,, ,, ,,	,, ,,	← 3·4 →		8	10	78 per cent. ,,	B, K, " Diene "	Kaufmann and Baltes.[23]
,, ,, ,,	,, ,, ,,	,,	4	—	9	10	77 per cent. ,,	C, F, S	Hilditch and Riley.[12]
,, ,, ,,	Suchumi ,, ,,	Russia	← 6 →		5	9	78 per cent. ,,		Taran.[59]
,, ,, ,,	Florida ,, ,,	Florida	← 4·6 →		1	—	95 per cent. ,,	B, K	McKinney and Jamieson.[24]
,, ,, ,,	,, ,, ,,	,,	← 4·6 →		4	1	91 per cent. ,,	B, K	,, ,, ,,[24]
,, ,, ,,	,, ,, ,,	U.S.A.	5	—	4	9	82 per cent. ,,	C, F, S	Hilditch and Riley.[12]
,, *moluccana*	Lumbang or candlenut	E. Indies	← 2·8 →		56	34	7 per cent. linolenic	L, H	West and Montes.[25]
,, syn. *triloba*	,, ,,	,,	← 2·1 →		41	49	8 per cent. ,,	L, H	Cruz and West.[26]
,, ,, ,,	,, ,,	,,	4·7	4·1(*e*)	32	35	24 per cent. ,,	F, T	Jamieson and McKinney.[27]
,, ,, ,,	,, ,,	Ceylon	0·7	4·3	35	33	27 per cent. ,,	L, T	Child.[60]
,, ,, ,,	,, ,,	Queensland	5·5	7	10·5	48·5	28·5 per cent. ,,	C, F, S	Gunstone and Hilditch.[75]
,, *trisperma*	Bagilumbang nut	E. Indies	← 17 →		13	—	67 per cent. α-elæostearic	B, K	McKinney and Jamieson.[28]
,, ,,	,, ,,	Java	← 18 →		12	19	51 per cent. ,,	" Diene "	Frahm and Koolhaas.[61]
Cephalocroton cordofanus		W. Sudan	← 2 →		59	6	33 per cent. ricinoleic	L	Henry and Grindley.[62]
Croton tiglium	Croton seed	Asia	1·3(*f*)	0·5	56	29	Traces lower acids	?	Flaschenträger and Wolffersdorff.[29]
Euphorbia calycina		Sudan	← 9 →		19	12	60 per cent. linolenic	L, T	Henry and Grindley.[63]
,, *erythraeæ*		Red Sea hills	← 13 →		7	39	41 per cent. ,,	L, T	,, ,, ,,[63]
,, *lathyris*	Caper spurge seed	Temperate	← 5·8 →		92	2	—	?	Sobol *et al.*[30]
Garcia nutans	Pinonchillo	Mexico	← 2 →		?	?	93–95 per cent. α-elæostearic	" Diene "	Jamieson and Rose.[64]
Hevea brasiliensis	Rubber seed	Brazil, etc.	7·4	9·2	29	33	21 per cent. linolenic	F, H	Jamieson and Baughman.[31]
,, ,,	,, ,,	,,	8·3(*g*)	8·6	30	30	21 per cent. ,,	F, T	Griffiths and Hilditch.[32]
,, ,,	,, ,,	Ceylon	11	12(*v*)	17	35	24 per cent. ,,	C F, S	Gunstone and Hilditch.[74]
,, ,,	,, ,,	Nigeria	9	10(*w*)	20	39	21 per cent. ,,	C, F, S	,, ,, ,,[74]
Jatropha curcas	Physic nut	Philippine Is.	11·9(*h*)	5·1	63·4	18·8	—	F	Cruz and West.[33]
,, ,,	,, ,,	India	15·6 (*t*)	9·7	40·9	32·1	—	F	Kartha and Menon.[71]
,, ,,	,, ,,	E. Indies	17·0	5·7	35·7	41.6	—	F	Steger and van Loon.[72d]
Joannesia princeps ¶	Anda-assu nut	Brazil	5·4 (*u*)	—	45·8	46·4	—	F, H	Gurgel and Ramos.[34]
,, ,,	,, ,,	,,	ca. 14	—	43	43	—	?	Pereira.[48]
Ricinodendron africanum	Essang seed	W. Africa	← 10·4 →		17	12	49 per cent. α-elæostearic and 11 per cent. linolenic.	B, K	Steger and van Loon.[35]
,, ,,	,, ,,	Nigeria	10	1	10	26	53 per cent. α-elæostearic	C, F, S	Hilditch and Riley.[12]
Ricinus communis	Castor seed	Sub-tropical	—	0·3(*i*)	7	4	88 per cent. ricinoleic	L, K	Panjutin and Rapoport.[36]
,, ,,	,, ,,	,,	← 2·4 (*q*) →		7	3	87 per cent. ,,	B, K	Kaufmann and Bornhardt.[65]
,, *zanzibarinus*		,,	← 1 →		Traces	8	91 per cent. ,,	B, T	Steger *et al.*[37]
Sapium sebiferum syn. *Stillingia sebifera*	Stillingia seed	China	6·3	2·8(*j*)	16	46	29 per cent. linolenic	F, T	Jamieson and McKinney.[38]
,, ,,	,, ,,	,,	← 6 →		9	59	26 per cent. ,,	B, T	Kaufmann and King.[66]
,, ,,	,, ,,	Florida	4·7	1·5(*k*)	12	53	28 per cent. ,,	F, T	Jamieson and McKinney.[38]
,, ,,	,, ,,	,,	← 7 →		5	67	21 per cent. ,,	B, T	Pye.[73]
Tetracarpidium conophorum	N'gart seed	Nigeria, 1943	4	3	13	17	63 per cent. linoleic	C, F, S	Gunstone and Hilditch.[76]
,, ,,	,, ,,	,, 1944	3	6	15	11	65 per cent. ,,	C, F, S	,, ,, ,,[76]

TABLE 51. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS OF THE FAMILIES ROSACEÆ, EUPHORBIACEÆ, AND CUCURBITACEÆ—continued*

Major component acids : OLEIC, LINOLEIC (sometimes LINOLENIC, ELÆOSTEARIC or other conjugated polyene acid, RICINOLEIC)
Minor component acids : Palmitic and Stearic.

		Habitat	Component Fatty Acids Per Cent. (Wt.)					Method	Observers
			Palmitic	Stearic	Oleic	Linoleic	Other Unsaturated Components		
CUCURBITACEÆ									
Cucumis Melo	Cantaloup (melon) seed	Tropics	10·3(*l*)	4·6	27·5	57·3	—	F, H	Baughman *et al.*[39]
„	„ „ „	India	7·3 (*x*)	0·2	43·1	45·1	—	F	Dhingra and Narain.[78a]
Cucurbita maxima	Hubbard squash	Sub-tropics	12·9	6·3	36·7	44·1	—	F, H	Baughman and Jamieson.[40]
(Citrullus) pepo	Pumpkin seed	„	← 30 →		25	45	—	L	Power and Salway.[41]
„ „	„ „	„	5·9	7·1	40·9	46·1	—	F	Riebsomer and Nesty.[42]
„ „	„ „	„	12	7	24	57	—	L, T	Kaufmann and Fiedler.[67]
„ *vulgaris*	Water melon seed	Tropics	12·6(*m*)	15·2	43	26	—	L	Pieraerts.[43]
„ „	„ „ „	Russia	11·3	10·2	13·4	65·2	—	F	Rankov and Popov.[68a]
„ „	„ „ „	„	11·4	10·1	14·7	63·7	—	F	„ „[68a]
„ „	„ „ „	India	7·6 (*y*)	6·1	35·3	48·7	—	F	Dhingra and Bisaras.[78b]
„ „ var. Cuban Queen.	„ „ „	Florida	9·2	5·8(*r*)	13·5	70·8	—	F	Nolte and Loesecke.[68b]
Echinocystis oregana	Wild cucumber seed	Sub-tropics	7·4	4·1	64	24	—	L, H	Einhorn *et al.*[44]
Hodgsonia capniocarpa	Kepayang seed	Malaya	37·3(*n*)	8·7	27·1	24·6	—	F	Hilditch *et al.*[45]
Lagenaria vulgaris	Seringe seed	India	←ca. 50 →		←ca. 50 →		—	?	Agarwal and Dutt.[46]
Luffa acutangula	Seed	India, W. Africa	← 30 →		28	42	—	?	Pieraerts and de Winter.[47]
„ *ægyptiaca*	Loofah seed	Africa, India	←ca. 20→		ca. 35	ca. 45	—	?	„ „[47]
Momordica charantia	—	India	—	16·3	83·7	—	—	?	Airan and Shah.[69]
„ *dioica*	—	„	—	16·9	83·1	—	—	?	„ „[69]
Telfairia occidentalis	Krobanko seed	Nigeria	16	3	23	23(*p*)	19 per cent. α-elæostearic	C, F, S	Hilditch and Riley.[12]
„ *pedata*	Koëme seed	E. Africa	26·4	19·9	12	35	6 per cent. linolenic	F, T	Smit and van Loon.[49]
„ „	„ „	„	32·5(*s*)	14·2	14	35·5	3 per cent. „	F, T	Hilditch and Meara.[70]
Trichosanthes cucumeroides	—	E. Indies	← 9 →		20	42	29 per cent. trichosanic ‡	L, K, "Diene"	Toyama and Tsuchiya[50]; Kaufmann *et al.*[51]
„ *Kadam*	Kadam seed	Tropics	ca. 20	—	ca. 80	—	—	?	Sack.[52]

(*a*) Also 1·2 per cent. myristic acid.
(*b*) Also 0·2 per cent. myristic and 0·8 per cent. arachidic acids.
(*c*) Also 1·8 per cent. myristic acid.
(*d*) Also 1·3 per cent. myristic acid.
(*e*) Also 0·1 per cent. arachidic acid.
(*f*) Also 11·3 per cent. myristic and 2·3 per cent. arachidic acids.
(*g*) Also 1·2 per cent. myristic and 0·3 per cent. arachidic acids.
(*h*) Also 0·5 per cent. myristic and 0·3 per cent. arachidic acids.
(*i*) Also 1·1 per cent. dihydroxystearic acid.
(*j*) Also 0·2 per cent. arachidic acid.
(*k*) Also 0·4 per cent. arachidic acid.
(*l*) Also 0·3 per cent. myristic acid.
(*m*) Also 2·5 per cent. lauric acid.
(*n*) Also 0·6 per cent. myristic, 0·8 per cent. arachidic, and 0·9 per cent. hexadecenoic acids.
(*o*) Also 1·8 per cent. myristic, 0·9 per cent. lignoceric, and 1·4 per cent. resin acids.
(*p*) Also 16 per cent. resin acids.
(*q*) Also 0·6 per cent. dihydroxystearic acid.
(*r*) Also 0·7 per cent. arachidic acid.
(*s*) Also 0·6 per cent. myristic acid.
(*t*) Also 1·4 per cent. myristic, 0·4 per cent. arachidic acids.
(*u*) Also 2·4 per cent. myristic acid.
(*v*) Also 1 per cent. arachidic acid.
(*w*) Also 1 per cent. arachidic acid.
(*x*) Also 4·3 per cent. myristic acid.
(*y*) Also 2·3 per cent. myristic acid.

* Licanic acid is 4-keto-$\Delta^{9,11,13}$-octadecatrienoic or 4-keto-elæostearic acid.
† Not less than 5 per cent. oleic acid.
‡ Trichosanic acid is apparently another geometrically isomeric form of α- and β-elæostearic acids.[50]
¶ Possibly a variety of *Aleurites triloba*.

Rosaceæ seed fats. For so large a botanical family, the data are, of course, relatively meagre. So far as they go, they fall into two well-defined groups:

(*a*) The shrubs of temperate or sub-tropical habitat (*Prunus*, *Rubus*, *Cratægus*, *Cydonia*), the seed fatty acids of which are mainly linoleic and oleic, with occasionally some linolenic acid, but usually with less than about 5 per cent. of saturated acids (mainly palmitic);

(*b*) Seed fats of the tropical genera *Licania* and *Parinarium*, in which the proportion of saturated acids is somewhat higher (usually 10–11 per cent.), oleic and linoleic acids are often present in only about the same amounts as the saturated acids, and the predominant components are highly unsaturated, conjugated C_{18} acids. α-Licanic (α-keto-elæostearic) is the main component (65–80 per cent. of the total acids) in the seed fats (oiticica oils) of *Licania rigida* (Brazil), *L. arborea* (Mexico), and *L. crassifolia* (East Indies) and of po-yoak fat from *Parinarium sherbroense* (West Africa). In *P. macrophyllum* seed fat about 30 per cent. of α-elæostearic acid is accompanied by less linoleic and more oleic, with about 14 per cent. of saturated (chiefly palmitic) acids. The seed fat of *P. laurinum* is at present almost unique in containing the conjugated tetraethenoid parinaric acid.

(Parinaric acid has also been observed by Tutiya [109] to be a constituent of balsam seed fat from *Impatiens balsamina*, a member of the family Balsaminaceæ indigenous to India and Japan. This is one of the few reports (*cf.* p. 170) of the occurrence of any of these conjugated polyethenoid acids in the seed fat of a plant belonging to a family other than Rosaceæ, Euphorbiaceæ, or Cucurbitaceæ.)

Euphorbiaceæ seed fats. The position here is not so simple as in Rosaceæ. Only one seed fat from the many species inhabiting cool regions has so far been studied in detail—the caper spurge, *Euphorbia lathyris*, which contains a very simple mixture of seed fatty acids with over 90 per cent. of oleic acid. The tropical species include both the ordinary type of "drying oil" seed fats (similar to those in Tables 49 and 50) and seed fats in which elæostearic acid is prominent; in *Aleurites* the two types of seed fatty acids are found in different species of the same genus. Throughout the whole group, the proportions of saturated acids are low, usually 4–10 per cent., although in one or two instances they rise to 15–18 per cent. of the total fatty acids.

Of the "normal" unsaturated seed fats (the components of which are quite in common with those listed in Tables 49 and 50), those of *Croton tiglium*, *Euphorbia calycina* and *E. erythraeæ*, *Hevea brasiliensis*, *Jatropha curcas*, *Joannesia princeps* and *Stillingia sebifera* may be instanced; in most of these linoleic and oleic are the only unsaturated component acids, but rubber seed oil also contains 15–20 per cent. of linolenic acid, so that it possesses "drying" properties, whilst some of the tropical *Euphorbia* seed fats contain still more linolenic acid. Candlenut or lumbang oil (*Aleurites moluccana* or *triloba*) also belongs to this group, containing, in addition to large proportions of oleic and linoleic acids, about 7 per cent. of linolenic acid.

Three other species of *Aleurites* (*A. cordata*, *Fordii*, and *montana*) are characterised by the presence of 75 per cent. or more of α-elæostearic acid in the seed glycerides (known as tung or China wood oils). These fats accordingly possess the property of ready gelation on heating owing to polymerisation of the conjugated triethenoid groupings, —CH:CH.CH:CH.

CH:CH—. The seed fat of the Mexican Pinonchillo tree *Garcia nutans* contains about 90 per cent. of elæostearic acid and is thus almost identical in composition with China wood or tung oil. Bagilumbang oil, from *A. trisperma*, contains slightly less α-elæostearic glycerides, but is otherwise evidently similar in type to the tung oils. The seed fatty acids of *Ricinodendron africanum* include about 50 per cent. of α-elæostearic acid with about 25 per cent. of linoleic acid and 10 per cent. each of oleic and palmitic acids.

The most recent studies[121] of fats of this group suggest that elæostearic and linoleic acids do not occur together in any seed fat so far examined, and that (whilst the proportions of linoleic and oleic acids show no correlation) the content of saturated (palmitic) acid has an inverse relationship to that of elæostearic acid.

The *Ricinus* seed fats are unique in their high content of ricinoleic acid, and also in the almost complete absence of any palmitic or other saturated acids ; Eibner and Münzing[48] give similar data to those in the table for the contents of ricinoleic, oleic, and linoleic acids and also record that stearic and dihydroxystearic acids together form 3 per cent. of the total acids.

Ricinoleic acid has elsewhere only been noted in quantity in the seed fat of the Sudanese *Cephalocroton cordofanus* and in that (ivory wood oil) of *Agonandra brasiliensis*, the latter belonging to the family Olacaceæ (*cf.* Table 50). The acid was formerly supposed to occur in some quantity in the oil of the grape seed (*Vitis vinifera*), but later work indicates that it is not a constituent, the earlier reports having been based on acetyl values of grape seed oils which had become partially hydrolysed into mono- and diglycerides.[49] Similarly the presence (*cf.* Table 50) of 10 per cent. of ricinoleic acid (as also of 6 per cent. of hexadecenoic acid) in argemone oil (from a Papaveraceous plant) seems unusual, and confirmation of this observation is desirable.

Cucurbitaceæ seed fats. These resemble those of Rosaceæ rather than those of Euphorbiaceæ in that nearly all species so far examined have seed fats whose component acids belong to the simple type of those in Table 50—abundant oleic and linoleic acids with subordinate amounts of palmitic and stearic acids. In a few instances the saturated acids approach about 30 per cent. of the total acids, and sometimes stearic acid is equally prominent with palmitic acid.

In two genera only have differences from this common mixture of fatty acids yet been encountered. Whilst the seed fat of *Telfairia pedata* is derived from the usual mixture of saturated, oleic, linoleic, and linolenic acids, that of *T. occidentalis* contains fairly large amounts of α-elæostearic and no linolenic glycerides. Similarly, the seed fat of *Trichosanthes cucumeroides* contains, in its component acids, about 30 per cent. of an isomeric form of elæostearic acid (*trichosanic acid*) in addition to oleic (20 per cent.), linoleic (42 per cent.), and saturated (8 per cent.) acids, although that of the related *T. Kadam* is apparently free from conjugated polyethenoid unsaturation.

Yet another isomeride of elæostearic acid, denominated *punicic acid*, was isolated by Toyama and Tsuchiya[50] from pomegranate seed oil (*Punica granatum*, family Punicaceæ or Lythrarieæ) ; Farmer and van den Heuvel[51] have confirmed the observation that punicic acid is a third naturally occurring isomeric form of elæostearic acid.

III. SEED FATS IN WHICH PALMITIC, AS WELL AS OLEIC AND LINOLEIC, ACID IS A MAJOR COMPONENT

Major component acids: **PALMITIC, OLEIC, LINOLEIC (in a few cases, stearic).**
Minor component acids: **(Myristic), stearic, (arachidic, lignoceric), linolenic.**

There are a very large number of oils whose component fatty acids include oleic and linoleic in much the same amounts as those in Table 50, but in which palmitic acid is also prominent. No sharp line of demarcation falls, of course, between oils of " minor " and " major " palmitic acid content; for the present purpose, as explained in Chapter I (p. 8), an acid is deemed to be a " major component " of a fat when it forms about 10 per cent. or more of the whole of the mixed fatty acids. Families with seed fats in which palmitic acid, as well as oleic and linoleic acids, is an important constituent include many herbaceous and shrubby types, and these have a definite tendency to be more regularly natives of sub-tropical and tropical regions than those falling within the categories of Tables 49 and 50; recorded detailed analyses for seed fat component acids of this type are collected in Table 52 (pp. 172-175). Another important group of seed fats belonging to this class is that of the Gramineæ, which it is convenient, however, to discuss separately (data in Table 53, p. 177); the Gramineæ, of course, are represented by many genera indigenous to temperate, as well as warmer, climes.

In the seed fats falling in Table 52, oleic and linoleic acids almost always still form 70 per cent. or more of the mixed fatty acids, an amount which is not greatly inferior to that of the oils in Tables 49 and 50; but the balance is made up to a marked extent of palmitic acid. Of the unsaturated acids, again, sometimes linoleic and sometimes oleic is the more in evidence; in quite a number of instances, including the abundant and technically valuable cottonseed oil, linoleic acid amounts to about 50 per cent. of the total acids, and such oils are, of course, characteristic members of the "semi-drying" class. It is in relatively few instances that the linoleic acid content falls much below 25-30 per cent., the oleic acid figure then rising proportionately to 50-60 per cent. or even higher.

The palmitic acid content of this group of seed fats seems to fall into two or three classes, somewhat as follows:

(i) In the families belonging to the Malvales (Malvaceæ, Tiliaceæ, Bombacaceæ), it is frequently in the region of about 20 per cent. of the total acids, and sometimes rises to considerably more than this figure. Cottonseed oils from different species and habitats (American, Egyptian, Indian) show extremely small variations in the amounts of their component acids, of which palmitic acid always forms about 20-22 per cent. It may be more than a coincidence that another seed fat belonging to the Malvales (that of *Theobroma cacao*, Sterculiaceæ) which has been studied in detail contains a similar proportion of palmitic acid (23 per cent.), although in this case stearic acid is present in still larger quantities (*cf.* Table 58, p. 194).

(ii) In contrast to this resemblance between the seed fats of many of the Malvales, it must be pointed out that other seed fats of similar high palmitic content belong to a variety of plant divisions and, equally, that families belonging to one and the same division yield seed fats whose major components are frequently quite different. The component acids of seed fats, in other words, are usually strongly specific with respect to the plant families,

TABLE 52. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS*

Major component acids: PALMITIC, OLEIC, LINOLEIC (in a few cases, stearic).
Minor component acids: (Myristic), stearic, (arachidic, lignoceric), linolenic.

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.)				METHOD	OBSERVERS
			PALMITIC	STEARIC	OLEIC	LINOLEIC		
BERBERIDACEÆ								
Akebia lobata	Akebi seed	Japan	23	2	53	22	L	Komori and Ueno.[1]
MENISPERMACEÆ								
Stephania tetranda	Hanfangchi seed	China	18·9	20·6 (*s'*)	51	8	F, H	Hsii.[6]
MAGNOLIACEÆ								
Illicium verum	Chinese star aniseed	,,	ca. 24·5	ca. 2·5	ca. 47·5	ca. 25·5	L, H	Bulir.[2]
,, ,,	,, ,, ,,	,,	—(*f'*)	7·9	63·3	24·4	F	Airan and Shah.[62]
,, *religiosum*	Japanese ,, ,,	Japan	ca. 23·5	ca. 2·5	ca. 63·5	ca. 10·5	L, H	Bulir.[2]
Michelia Champaca	Seed	E. Indies	ca. 30	—	ca. 70	—	?	Sack.[3]
Schizandra chinensis	—	Russia	←— 9 —→		29–35	62–56	?	Balandin.[64]
ANONACEÆ								
Anona muricata	Guanabana seed	Puerto Rico	17·6 (*g'*)	6·0	63·5	12·6	F	Asenjo and Goyco.[65]
,, *squamosa*	Sirikaya seed	Tropics	14·8	10·7 (*a*)	18·2	55·4	F, H	Ghanekar and Ayyar.[4]
,, ,,	Sugar apple	Japan	←— 39 —→		29	32	L	Hata.[52]
Asimina triloba	Papaw seed	U.S.A.	2·5	2·0 (*r'*)	65·3	28·6	F	Riebsomer *et al.*[66]
RUTACEÆ								
Ægle marmelos	Bael seed	Ceylon	16·6	8·8	30	39 (*t'*)	F, T	Child.[63]
Citrus Aurantium	Orange seed	S. California	20·7	4·7 (*u'*)	36·5	36·5	F, T	Van Atta and Dietrich.[7]
,, *decumana*	Grape fruit seed	Sub-tropics	20·2	7·5 (*b*)	20·7	51·4	F	Jamieson *et al.*[5]
,, ,, var. Foster	,, ,, ,,	Trinidad	28·9 (*c''*)	2·1	25·1	36·6	C, F, S	Hilditch and Riley.[84]
,, ,, var. Marsh	,, ,, ,,	,,	27·5 (*d''*)	2·9	21·1	39·3	C, F, S	Hilditch and Riley.[84]
,, ,,	Indian shaddock	India	20·7	15·3	55·4	8·1 (*h'*)	?	Rao *et al.*[67]
ANACARDIACEÆ								
Anacardium occidentale	Cashew nut	Tropics	6·4	11·3	74·1	7·7	F	Patel *et al.*[8]
,, ,,	,, ,,	,,	4·1	5·8 (*c*)	68·2	21·7	F	Ichaporia.[9]
Anthrocaryon Nannani	Gonyo almond	Congo	13·5 (*d*)	10·5	45·5	24·5	L, H	Pieraerts and Ipatiev.[10]
Buchanania latifolia	Seed	India	28·9 (*k'*)	8·1	57·4	5·5	F	Gunde and Srivastava.[69]
Mangifera Indica	Mango	,,	8·8	34·0 (*b''*)	49·8	—	F	Pathak *et al.*[83]
Pistacia lentiscus	Shinia nut	Levant	27	13	53	7	?	Vodret.[11]
,, *vera*	Pistachio nut	Asia	19	—	60	21	L, H	Beythien.[12]
,, ,,	,, ,,	India	8·2 (*e*)	1·6	69·6	20·0	F	Dhingra and Hilditch.[13]

TILIACEÆ								
Corchorus capsularis	Jute seed	Tropics	←— 20 —→		37	43	L, H	Sen.[14]
Tilia parvifolia	Lime seed	Temperate zones	←— 13 —→		29	58	B, T	Kaufmann and Fiedler.[15]
MALVACEÆ								
Aboutilon theophrasti	Buttonweed seed	U.S.A.	12·8 (*e″*)	0·9	14·8	60·9	F	Carmody *et al.*[85]
Gossypium arboreum,	Cottonseed	India	19·9 (*f*)	1·3	29·6	45·3	F	Hilditch and Jones.[16]
herbaceum, etc.	„	„	19·6 (*g*)	2·7	24·6	50·4	F	Hilditch and Rhead.[17]
„ „	„	„	23·4 (*v′*)	1·1	22·9	47·8	F	Hilditch and Maddison.[68]
„ *barbadense*	„	U.S.A. Sea Island	20·2 (*h*)	2·0	35·2	41·7	F, H	Jamieson and Baughman.[18]
„ *hirsutum*	„	U.S.A. Upland	21·9 (*i*)	1·9	30·7	44·9	F	Jamieson and Baughman.[19]
„ „	„	„ „	23·4	—	23·0	53·6	F	Armstrong and Allan.[20]
„ „	„	U.S.A.	←—27—→		19	54	T	Mitchell *et al.*[77]
„ „	„	„	←—27—→		18	55	S	„ „[77]
Hibiscus cannabinus	Kenaph seed	Egypt, India	15·8	6·8	51·0	26·4		Bauman.[21]"
„ *esculentus*	Okra seed	Tropics	26·9	2·7 (*j*)	43·7	26·6	F, H	Jamieson and Baughman.[22]
„ *moscheutos × H. coccineus.*	Rose mallow seed		←— 16·5 —→		42·5	41	F, T	Barkenbus and Thorn.[23]
BOMBACACEÆ								
Adansonia Grandidieri	Baobab kernel	Madagascar, India	37 (*l*)	2	42	10·0	L (?)	Thomas and Boiry.[24]
Bombax malabaricum	Kapok seed	India	23·6 (*z′*)	—	64·9	7·5	F	Rao *et al.*[80]
Ceiba pentandra, syn.	} Kapok seed	Tropics	26	—	44·5	29·5	L	Trevithick and Dickhart.[25]
Eriodendron anfractuosum	„ „	„	16·1 (*m*)	2·3	50·6	29·7	F	Cruz and West.[26]
„ „	„ „	Java	10·5	8·5 (*n*)	46·1	33·6	F	Jamieson and McKinney.[27]
„ „	„ „	Japan	←— 16·5 —→		51	32·5	L	Mehlenbacher.[28]
Pachira aquatica	Pachira kernel	Congo	46	—	43	11	L	Pieraerts *et al.*[29]
CARYOCARACEÆ								
Caryocar villosum	Piqui-a	Brazil	48·4 (*o*)	0·9	46·0	3·3	F	Hilditch and Rigg.[30]
CARICACEÆ								
Carica papaya	Melon tree seed	S. America	12·0	5·5 (*p*)	80·0	2·2	F	von Loesecke and Nolte.[31]
„ „	Papaya seed	Florida	13·0 (*w′*)	1·8	80·6	—	F, H	Asenjo and Goyco[78]
LECYTHIDACEÆ								
Bertholletia excelsa, nobilis	Brazil nut	Brazil	14·3 (*q*)	2·7	58·3	22·8	F, H	Schuette *et al.*[32]
„ „ „	„ „	„	15·4 (*r*)	6·2	48·0	29·8	F, H	Schuette and Erz.[33]
COMBRETACEÆ								
Quisqualis indica	Seed	China	29·2 (*l′*)	9·1	49·2	10·0	F, T	Kaufmann and King.[70]
Terminalia catappa	Talisay seed	E. Indies	29·0 (*s*)	4·1	41·7	23·4	F	Cruz and West.[34]
„ „	„ „	W. Africa	34·0	9·7 (*t*)	27·3	28·6	F	Ichaporia.[9]
„ „	Tropical almond	Philippines	38·9 (*m′*)	4·0	37·3	19·1	F	Asenjo and Goyco.[71]
„ *chebula*	Myrobalan seed	India	←— 18 —→		59	23	L	Sunthankar and Jatkar.[35]

TABLE 52. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS—continued.*

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.) PALMITIC	STEARIC	OLEIC	LINOLEIC	METHOD	OBSERVERS
APOCYNACEÆ								
Cerbera odollam	Seed	India, Pacific	30·1	9·9 (*u*)	42·6	16·5	F, H	Ghanekar and Ayyar.[36]
Holarrhena antidysenterica	,,	Tropical Asia	5·6	6·8 (*v*)	21·0	54·7	F, H	Ghanekar and Ayyar.[37]
Strophanthus hispidus	,,	Africa	15	7	62	16	L, H	Matthes and Rath.[38]
Thevetia neriifolia	,,	India	17·1	11·8 (*w*)	64·4	6·3	F, H	Bhattacharya and Ayyar.[39]
SOLANACEÆ								
Atropa belladonna	Belladonna seed	Europe, etc.	5·9	1·8	25·5	66·8	F	Hilditch and Ichaporia.[40]
Datura alba	Datura seed	E. Africa	7	—	65	28	L, H	Dieterle.[41]
,, *stramonium*	Thorn apple seed	Tropics	12	2	41	45	L, H	Meyer and Beer.[42]
,, ,,	,, ,, ,,	,,	11	2	←— 87 —→		B	Verkade and Coops.[43]
,, ,,	,, ,, ,,	,,	←— 11·5 —→		27·5	61	B, T	Lutenberg and Ivanov.[44]
,, ,,	,, ,, ,,	,,	10·8 (*x*)	1·2	33·1	53·6	F	Hilditch and Ichaporia.[40]
Hyoscyamus niger	Henbane seed	Europe, etc.	←— 10 —→		16	74	B, T	Lutenberg and Ivanov.[45]
,, ,,	,, ,,	,,	6·5	0·4	11·1	82·0	F	Hilditch and Ichaporia.[40]
,, ,,	,, ,,	India	6·5 (*a″*)	1·6	35·2	56·4	F	Pathak *et al.*[81]
Nicotiana tabacum	Tobacco seed	Tropics, etc.	10	—	24	66	?	Piatnitzki.[46]
,, ,,	,, ,,	Wisconsin, U.S.A.	3·3	5·1	17·1	74·5	F	Roberts and Schuette.[47]
,, ,,	,, ,,	Connecticut, U.S.A.	9·8	5·9	28·0	56·3	F	Salisbury.[48]
,, ,,	,, ,,	Philippine Is.	7·2 (*y*)	3·1	27·2	62·0	F	Cruz and West.[49]
,, ,,	,, ,,	Madras	7·8 (*y′*)	5·6	30·2	54·6	F	Venkatarao *et al.*[79]
,, ,,	,, ,,	U.S.A.*	7	3	15	75	C, F, T	Riemenschneider *et al.*[82]
Physalis peruviana	Cape gooseberry seed	India	7·2	6·0	46·1	40·7	F	Gupta and Lal.[50]
Solanum esculentum syn.	Tomato seed	Temperate zones	13	6 (*z*)	46	35	L	Rabak.[51]
,, *lycopersicum*	,, ,,	Formosa	←— 22 —→		16	62	L	Hata.[52]
,, *indicum*	—	India	7·2	6·6 (*n′*)	35·5	49·5	F	Puntambekar and Krishna.[72]
,, *nigrum*		,,	←— 6 —→		69	25	L	Pendse.[53]
,, *xanthocarpum*		,,	5·7	10·3 (*a′*)	45·4	38·2	F	Gupta and Dutt.[54]
MARTYNIACEÆ								
Martynia diandra	Unicorn seed	India	9·1	12·7 (*p′*)	40·3	36·4	F	Tayal and Dutt.[73a]
,, ,,	Devil's claw	,,	10·5	8·5	74·5	5·5	F	Airan and Shah[73b]
ACANTHACEÆ								
Blepharis edulis		India	←— 12 —→		73·5	14·5	L	Pendse and Lal.[55a]
Hygrophyla spinosa		,,	18·3 (*b′*)	5·3	←— 75·0 —→		F	Phalnikar *et al.*[55b]
,, ,,		,,	5·4 (*o′*)	11·9	9·8	71·5	F	Godbole *et al.*[74]

* Average of 12 analyses of tobacco seed oils of different types of varieties.

RUBIACEÆ								
Coffea arabica	Coffee seed	Tropical Asia, America, etc.	35	—	2·5	62·5	L, H	Meyer and Eckart.[56]
,, ,,	,, ,,	,, ,,	28·2 (c′)	12·7	17·3	35·8	F	Schuette *et al.*[57]
,, ,,	,, ,,	,, ,,	24·3 (d′)	1·1	20·8	38·7	F	Heiduschka and Kühn.[58]
,, ,,	,, ,,	,, ,,	←— 44 —→		31	25	B	Bauer and Neu.[59a]
,, ,,	,, ,,	Brazil	←— 36 —→		35	39	B	Bauer and Neu.[59b]
CAPRIFOLIACEÆ								
Sambucus canadensis	Elderberry	Canada	5·8	2·8 (q′)	4	53	F, T	Schuette *et al.*[75]
,, *racemosa*	,,	General	23	—	45	25 (e′)	L, H	Matthes and Rossié.[60]
,, ,,	,,	,,	←— 17·5 —→		←— 82·5 —→		L	Thoms.[61]
Viburnum dentatum	Arrow wood	U.S.A.	5·4 (x′)	1·3	65·5	23	F	Schuette *et al.*[76]
,, *opulus* var. *americanum*	Highbush cranberry	,,	←— 1·7 —→		60·8	37·5	L	Schuette and Korth.[76]

(a) Also 0·9 per cent. lignoceric acid.
(b) Also 0·2 per cent. lignoceric acid.
(c) Also 0·2 per cent. arachidic acid.
(d) Also 6·0 per cent. myristic acid.
(e) Also 0·6 per cent. myristic acid.
(f) Also 3·3 per cent. myristic and 0·6 per cent. arachidic acids.
(g) Also 2·0 per cent. myristic and 0·7 per cent. arachidic acids.
(h) Also 0·3 per cent. myristic and 0·6 per cent. arachidic acids.
(i) Also 0·5 per cent. myristic and 0·1 per cent. arachidic acids.
(j) Also 0·1 per cent. arachidic acid.
(l) Also 8·7 per cent. myristic acid ; and 11 per cent. " lactones " not allowed for in the above analysis.
(m) Also 0·5 per cent. myristic and 0·8 per cent. arachidic acids.
(n) Also 1·3 per cent. arachidic and traces of lignoceric acid.
(o) Also 1·4 per cent. myristic acid.
(p) Also 0·3 per cent. arachidic acid.
(q) Also 1·9 per cent. myristic acid.
(r) Also 0·6 per cent. myristic acid.
(s) Also 1·0 per cent. myristic and 0·8 per cent. arachidic acids.
(t) Also 0·4 per cent. arachidic acid.
(u) Also 0·9 per cent. lignoceric acid.
(v) Also 1·9 per cent. lignoceric and 10·0 per cent. linolenic acids.
(w) Also 0·4 per cent. arachidic acid.
(x) Also 1·3 per cent. myristic acid.
(y) Also 0·1 per cent. myristic and 0·4 per cent. arachidic acids.
(z) Also 0·4 per cent. arachidic acid.
(a′) Also 0·4 per cent. arachidic acid.
(b′) Also 1·4 per cent. myristic acid.
(c′) Also 3·1 per cent. myristic and 2·9 per cent. arachidic acids.
(d′) Also 0·4 per cent. decanoic and 14·7 per cent. carnaubic (!) acids.
(e′) Also traces of arachidic and 7 per cent. linolenic acids.
(f′) Also 4·4 per cent. myristic acid.
(g′) Also 0·3 per cent. myristic acid.
(h′) Also 0·5 per cent. linolenic acid.
(k′) Also 0.1 per cent. myristic acid.
(l′) Also 4·5 per cent. myristic acid.
(m′) Also 0·7 per cent. myristic acid.
(n′) Also 1·2 per cent. arachidic acid.
(o′) Also 1.4 per cent. myristic acid.
(p′) Also 1·5 per cent. arachidic acid.
(q′) Also 34 per cent. linolenic acid.
(r′) Also 1·6 per cent. arachidic acid.
(s′) Also 0·2 per cent. arachidic and 1 per cent. linolenic acid.
(t′) Also 6 per cent. linolenic acid.
(u′) Also 0·9 per cent. arachidic and traces of linolenic acids.
(v′) Also 1·4 per cent. myristic, 1·3 per cent. arachidic and 2·1 per cent. hexadecenoic acids.
(w′) Also 4·6 per cent. myristic acid.
(x′) Also 0·4 per cent. myristic and 4·4 per cent. hexadecenoic acids.
(y′) Also 1·8 per cent. myristic acid.
(z′) Also 1·2 per cent. myristic and 2·8 per cent. arachidic acids.
(a″) Also 0·3 per cent. myristic acid.
(b″) Also 0·7 per cent. myristic and 6·7 per cent. arachidic acids.
(c″) Also 0·8 per cent. myristic, 0·6 per cent. arachidic and 5·9 per cent. linolenic acids.
(d″) Also 1·2 per cent. myristic, 2·1 per cent. arachidic and 5·9 per cent. linolenic acids.
(e″) Also traces of myristic and linolenic, and 10·0 per cent. C_{20} (or higher) acids.

but not always in regard to the wider groups into which the families have been collected on botanical grounds.

Other families, in addition to those mentioned, in which palmitic acid usually forms about 20 per cent. or more of the seed fats, appear to include Menispermaceæ and Magnoliaceæ (Ranales), Rutaceæ and Burseraceæ (Table 58, p. 195) (Geraniales), Caryocaraceæ (Parietales), Combretaceæ and perhaps Lecythidaceæ (Myrtifloræ), Rubiaceæ and Caprifoliaceæ (Rubiales). In practically all these instances the amount of any other saturated acid present is of quite a minor order. The palmitic acid content (48 per cent.) of piqui-a kernel fat (*Caryocar villosum*) is one of the highest yet observed in a seed fat.

(iii) In the Solanaceæ (data for which are incidentally more abundant than in many of the other families) the seed fat content of palmitic acid is usually nearer 10 per cent. than 20 per cent. of the total acids. In this respect, and still more in the abundance of oleic and linoleic acids and the absence of other saturated acids, Solanaceæ seed fats form a very similar group to those of most of the Cucurbitaceæ, but in this case the two plant families have no close botanical connection.

(iv) Finally, in some of the families (Anacardiaceæ, Apocynaceæ, Anonaceæ, Martyniaceæ), the palmitic acid content of seed fats is somewhat variable and, in several of the examples, stearic acid is recorded in amounts approaching or even exceeding 10 per cent. of the total acids. Such seed fats are, more strictly speaking, intermediate between the class now under discussion and that (Table 58) in which, in a few tropical families, stearic acid becomes a prominent feature of the seed fat. It is rather obvious that decrease in linoleic acid does not necessarily accompany the appearance of stearic acid in such cases ; indeed, although in some cases (e.g. cashew and shinia nuts) the proportion of linoleic acid is very low, in others (such as the seed fat of *Anona squamosa*) it forms over half of the total acids in spite of the presence of 11 per cent. of stearic and 15 per cent. of palmitic acid. It is accordingly, at present, doubtful whether any correlation can be detected between the presence of stearic acid, and diminution in linoleic acid, in seed fats.

IIIA. SEED FATS OF THE GRAMINEÆ

Major component acids: OLEIC, LINOLEIC, PALMITIC.
Minor component acids: Stearic (occasionally myristic, arachidic, linolenic).

The available data in this class, which are shown in Table 53, are of interest not only because they include analyses of the oils present in the common and important cereals wheat, barley, rice, oats, and maize, but also because they afford instances in which endosperm fats have been examined separately from those of the embryo. The embryo or germ, in the Gramineæ, usually contains much more fatty matter than the corresponding endosperm ; thus, in wheat the embryo contains 10–17 per cent. of fat, and the endosperm only 1–2 per cent., whilst for rye the respective figures are 8–11 per cent. and 1–3 per cent., and for rice, up to 35 per cent. and 8–12 per cent.

The respective embryo and endosperm fats, so far as can be judged from the analyses in Table 53, are not very different in any given species, but there seems to be a very definite distinction in the relative amounts of oleic,

TABLE 53. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS OF THE GRAMINEÆ*

Major component acids : OLEIC, LINOLEIC, PALMITIC.
Minor component acids: Stearic (occasionally myristic, arachidic, linolenic).

		Habitat	Component Fatty Acids per Cent. (Wt.)				Method	Observers
			Palmitic	Stearic	Oleic	Linoleic		
Andropogon sorghum	Sorghum	Manchuria	28	—	ca. 48	ca. 24	L	Ueno and Kuzei.[1]
Avena sativa	Oat (germ)	Temperate zones	10	—	59	31	L, H	Amberger and Hill.[2]
Hordeum vulgare	Barley (seed)	,, ,,	9	3	33	54 (*a*)	L, H	Täufel and Rusch.[3]
,, ,,	,, (germ) (malt)	,, ,,	10	6	21	62 (*b*)	L, H	,, ,, [3]
Oryza sativa	Rice (meal)	Tropics	13·2 (*c*)	1·9	44·1	39·4	F	Jamieson.[4]
,, ,,	,, (bran)	,,	←— 17·5 —→		42·5	40	L	A.O.C.S.[5]
,, ,,	,, (bran)	Philippine Islands	18·0 (*d*)	2·8	48·2	29·4	F	Cruz, West, and Aragon.[6]
,, ,,	,,	Japan	←— 13 —→		52	35	L	Ueno and Ueda.[7]
Panicum miliaceum	Millet	Sub-tropics	←— 12 —→		24·5	58 (*e*)	B, T	Steger and van Loon.[8]
Secale cereale	Rye (seed)	Temperate zones	←— 21 —→		18	61	L, H	Croxford.[9]
,, ,,	,, (germ)	,, ,,	2·5	8·8 (*f*)	33	52·5	F	Stout and Schuette.[10]
Setaria italica	Foxtail millet (bran)	Manchuria	←— 10 —→		9	81	L	Mano, Yoshiketsu.[14]
Triticum vulgare	Wheat (germ)	Temperate zones	13·8	1·0 (*g*)	30	49	F, T	Jamieson and Baughman.[11]
,, ,,	,, (germ)	,, ,,	11·8	3·0 (*h*)	39	30	F, T	Sullivan and Bailey.[12]
,, ,,	,, (germ)	,, ,,	←— 15·5 —→		25·5	53 (*k*)	B, T	Radlove.[16]
,, ,,	,, (germ)	,, ,,	16	6	12	57 (*l*)	C, F S	Gunstone and Hilditch.[17]
Zea Mays	Maize (germ)	Sub-tropics	7·8	3·5 (*i*)	46·3	41·8	F, H	Baughman and Jamieson.[13]
,,	,, (germ)	U.S.A.	10·2	3·0 (*j*)	49·6	34·3	F	Longenecker.[15]
,,	,, (germ)	,,	8·1 (*m*)	2·5	30·1	56·3	F, T	Baur and Brown.[18]

(*a*) Also 0·5 per cent. linolenic acid.
(*b*) Also 1 per cent. linolenic acid.
(*c*) Also 0·3 per cent. myristic, 0·6 per cent. arachidic, and 0·5 per cent. lignoceric acids.
(*d*) Also 0·1 per cent. myristic, 0·5 per cent. arachidic, and 1·0 per cent. lignoceric acids.
(*e*) Also 5·5 per cent. linolenic acid.
(*f*) Also 0·2 per cent. arachidic and 3 per cent. linolenic acids.
(*g*) Also 0·3 per cent. lignoceric and 6 per cent. linolenic acids.
(*h*) Also 1·2 per cent. lignoceric and 15 per cent. linolenic acids.
(*i*) Also 0·4 per cent. arachidic and 0·2 per cent. lignoceric acids.
(*j*) Also 1·4 per cent. myristic and 1·5 per cent. hexadecenoic acids.
(*k*) Also 6 per cent. linolenic acid.
(*l*) Also 9 per cent. linolenic acid.
(*m*) Also 0·1 per cent. myristic, 1·2 per cent. hexadecenoic, and 1·7 per cent. unsaturated acids above C_{18}.

linoleic and linolenic acids present in the seed fats of the various genera of the Gramineæ. Linolenic acid is reported in the case of wheat, millet, rye, and barley seed fats (especially in wheat germ fat) and the proportion of oleic acid in these fats (all of which are denizens of temperate climatic regions) is definitely lower than in those of the sub-tropical maize or the tropical rice; on the other hand, the embryo fat of the oat resembles the latter in being rich in oleic and lower in linoleic acid components. Any effect due to purely climatic influences is thus, as in previous cases, apparently obscured by some other influence of a specifically biological nature.

The content of saturated acids (almost all palmitic) of the Gramineæ seed fats is usually in the region of 10–15 per cent., but occasionally approaches or exceeds 20 per cent.

SEED FATS CONTAINING CHARACTERISTIC ACIDS OTHER THAN, OR IN ADDITION TO, OLEIC, LINOLEIC, AND PALMITIC ACIDS

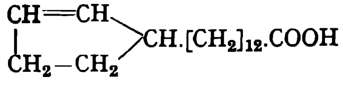
In passing from the fats in which oleic, linoleic (linolenic), and palmitic acids are the only major components to those in which one or more other acids are present in substantial proportions, the close connection between seed fat composition and the family to which the parent plant belongs becomes still more evident. The fatty acids which appear individually in quantity in certain seed fats are:

(i) unsaturated: petroselinic, tariric, octadecendiynoic, eicosenoic, erucic, hexacosenoic, tricosenoic, chaulmoogric, and hydnocarpic, elæostearic, keto-elæostearic, parinaric, ricinoleic.

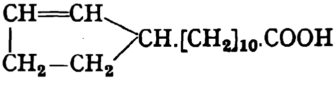
(ii) saturated: arachidic and lignoceric, stearic, myristic, lauric, (or both of the latter together).

(a) SEED FATS CONTAINING SPECIFIC UNSATURATED ACIDS

The fats in which *elæostearic* acid and its natural isomeric forms, $CH_3.[CH_2]_3.[CH:CH]_3.[CH_2]_7.COOH$, 4-keto-elæostearic acid, $CH_3.[CH_2]_3.[CH:CH]_3.[CH_2]_4.CO.[CH_2]_2.COOH$, parinaric acid, $CH_3.CH_2.[CH:CH]_4.[CH_2]_7.COOH$, and ricinoleic acid, $CH_3.[CH_2]_5.CH(OH).CH_2.CH:CH.[CH_2]_7.COOH$, are present in large amounts have already received attention (Table 51). The other examples of unsaturated major components known up to the present include the mono-acetylenic *tariric* acid, $CH_3.[CH_2]_{10}.C{:}C.[CH_2]_4.COOH$, an acid $C_{18}C_{26}O_2$ with one ethenoid (terminal vinyl) group and two acetylenic linkings, and the following mono-ethylenic acids: *petroselinic*, $CH_3.[CH_2]_{10}.CH:CH.[CH_2]_4.COOH$, an eicosenoic acid, $CH_3.[CH_2]_5.CH:CH.[CH_2]_9.COOH$, *erucic* acid, $CH_3.[CH_2]_7.CH:CH.[CH_2]_{11}.COOH$, *ximenic* acid, $CH_3.[CH_2]_7.CH:CH.[CH_2]_{15}.COOH$, *lumequic* acid, $CH_3.[CH_2]_7.CH:CH.[CH_2]_{19}.COOH$, and *chaulmoogric* and *hydnocarpic* acids.* The latter are cyclopentene derivatives of the formulæ:



Chaulmoogric acid



Hydnocarpic acid

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* To the above list should be added the peculiar main component acid of the seed fats of *Sterculia fœtida* (and perhaps some other *Sterculia* species), which has the formula $C_{19}H_{34}O_2$ and is apparently a 12-methyl-$\Delta^{9,11}$-octadecadienoic acid (*cf.* p. 197).

Each of these unsaturated acids is associated with the seeds of only one or two families of plants, as will be seen from the descriptions which follow.

SEED FATS WITH PETROSELINIC (Δ^6-OCTADECENOIC) ACID AS MAJOR COMPONENT

Major component acids: PETROSELINIC, OLEIC, LINOLEIC.
Minor component acids: Palmitic.

The occurrence of unsaturation in the Δ^6 position of the C_{18} chain, in contrast to or accompanying the Δ^9 ethylenic linking common to oleic, linoleic and linolenic acids, is comparatively uncommon, except in the seed fats of the Umbelliferæ and of ivy and one or two other species of plants. In umbelliferous plants, however, the Δ^6-octadecenoic acid seems invariably to be a major component.

It may here be interpolated that the triethenoid C_{18} acid present in the the seed fat of the evening primrose (Œnotheraceæ) is $\Delta^{6, 9, 12}$-octadecatrienoic acid,[52] and is thus related to the mono-ethenoid petroselinic acid in the same way that ordinary linolenic acid is to oleic acid. Again, the acetylenic tariric acid, Δ^6-octadecynoic acid, the occurrence of which is discussed below, is structurally related to petroselinic and not to oleic acid.[53]

The observation of Vongerichten and Köhler [55] in 1909 that parsley seed oil contained over 70 per cent. of a Δ^6-octadecenoic acid (petroselinic acid) was confirmed in 1927 by Hilditch and (Miss) Jones,[56] and by van Loon.[57] Subsequent examination of the seed fats from eight other species of umbelliferous genera disclosed the presence in every instance of petroselinic acid in amounts varying from 19 to 60 per cent. of the total fatty acids of the oils (*cf.* Table 54, p. 180). The other acids present were oleic and linoleic in varying proportions, together with minor amounts (usually 3–4 per cent.) of palmitic, the only saturated acid. Chervil seed oil appears peculiar in its high content of linoleic acid coupled with substantial absence of oleic acid, and this feature is perhaps worth further study.

Petroselinic acid has thus been observed in quantity in every umbelliferous seed fat so far analysed, but its presence has hitherto only been reported in the seeds of plants belonging to two other families, Araliaceæ (a closely allied Umbellate family, classified separately on account of the more succulent fruit) and one genus from the Simarubaceæ.

The fat of ivy (*Hedera helix*, Araliaceæ) seeds was stated to contain petroselinic acid by Palazzo and Tamburello [58] in 1914, and this observation was confirmed by the detailed analysis of Steger and van Loon [59] in 1928.

Tsujimoto and Koyanagi [60] have observed that the 77 per cent. of unsaturated acids from Nigaki seed fat (*Picrasma quassioides*, Simarubaceæ) consist for the greater part of petroselinic acid.

SEED FATS WITH TARIRIC ACID (OR OTHER ETHYNOID ACID) AS MAJOR COMPONENT

Tariric (Δ^6-octadecynoic) acid was first reported by Arnaud [53] in 1892 as a component of the seed fat of *Picramnia tariri* and was later observed in those of *P. Camboita* and *P. Carpinteræ*,[61] these species being indigenous to

TABLE 54. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS OF THE UMBELLIFERÆ AND ARALIACEÆ*

Major component acids: All unsaturated—OLEIC, LINOLEIC, and PETROSELINIC.
Minor component acids: Palmitic.

		COMPONENT FATTY ACIDS PER CENT. (WT.)				METHOD	OBSERVERS
		PALMITIC	OLEIC	LINOLEIC	PETROSELINIC		
UMBELLIFERÆ *							
Angelica sylvestris	Angelica	4	44	33	19	F	Hilditch and (Miss) Jones.[1]
Anthriscus cerefolium	Chervil	5	0·5	53·5	41	F	Christian and Hilditch.[2]
Apium graveolens	Celery	3	26	20	51	F	" " [2]
Carum carvi	Caraway	3	40	31	26	F	" " [2]
Coriandrum sativum	Coriander	8	32	7	53	F	" " [2]
Daucus carota	Carrot	4	14	24	58	F	" " [2]
Fœniculum officinale	Fennel	4	22	14	60	F	" " [2]
Heracleum sphondylium	Hogweed	4	52	25	19	F	Hilditch and (Miss) Jones.[1]
Pastinaca sativa	Parsnip	1	32	21	46	F	Christian and Hilditch.[2]
Petroselinum sativum	Parsley	3	15	6	76	F	Hilditch and (Miss) Jones.[3]
		3	9	18	70	L, H	van Loon.[4]
ARALIACEÆ *							
Hedera helix	Ivy	5	20	13	62	L, H	Steger and van Loon.[5]

* All the species mentioned grow in temperate or sub-tropical regions.

Guatemala, Guiana, or Brazil. Grimme [62] found that the component acids of the seed fat of *P. Lindeniana* (Guatemala) consisted approximately of myristic 22, palmitic 33, stearic 3, oleic 22, and tariric 20 per cent., acids. The fatty acids from the seed fat of yet another species of *Picramnia*, *P. Sow*, were, however, found by Steger and van Loon [63] to consist almost wholly (nearly 95 per cent.) of tariric acid; these authors confirmed the structure of the acid as Δ^6-octadecynoic acid, $CH_3.[CH_2]_{10}.C{:}C.[CH_2]_4.COOH$.

The occurrence of this acetylenic acid is at present confined to the one Central American genus *Picramnia*, a member of the family Simarubaceæ (sub-family Terebinthaceæ). The seed fats of other plants belonging to the Simarubaceæ are quite different, and somewhat variable, in their component acids (see Table 59A and pp. 199, 201).

Reference should again be made here to the rare di-unsaturated C_{18} acid, with two acetylenic and one ethylenic (terminal vinyl) linkings, isolated from the seed fat of a species of *Ongokea* (Olacaceæ) by Steger and van Loon and other workers.[54]

SEED FATS WITH CYCLIC UNSATURATED ACIDS (CHAULMOOGRIC, HYDNOCARPIC, GORLIC) AS MAJOR COMPONENTS

Flacourtiaceæ Seed Fats

Chaulmoogric and hydnocarpic acids, the C_{16} and C_{18} acids containing a cyclopentene group whose structural formulæ were given on p. 178, are present in quantity in the seed fats of many members of this family; moreover, so far as at present known, they do not seem to occur elsewhere. These acids contain an asymmetric carbon atom and are thus capable of existence in optically active forms; actually, the naturally occurring chaulmoogric and hydnocarpic glycerides are strongly dextro-rotatory. The acids also possess marked therapeutic properties and are valuable medicinally, especially in the treatment of leprosy.

A diethenoid cyclopentene acid, gorlic acid, $C_{18}H_{30}O_2$, has been observed in some cases [64] to accompany chaulmoogric acid in smaller quantities than the latter: in gorlic acid one ethylenic linking is in the cyclopentene ring (as in chaulmoogric acid), whilst the other is in the aliphatic chain (13-Δ^2-*cyclo*pentenyl-Δ^6-tridecenoic acid).[65]

Members of this family are found in tropical regions in Asia, Africa, and Central and South America.

Until recently, quantitative methods for determination of chaulmoogric and hydnocarpic acids in admixture with oleic, linoleic, palmitic, etc., acids were unavailable, but recently Cole and Cardoso [66a] have given detailed figures for five of the Flacourtiaceæ seed fats of the chaulmoogra type. Table 55 (p. 182), in addition to these data, includes a summary of most of the Flacourtiaceæ seed fats which may serve to indicate in a general manner the extent to which the cyclic acids are present, and also to demonstrate their absence from some species (although other species, even of the same genus, may develop them in abundance in their seeds).

Cole and Cardoso [66b] have also established that very small quantities of lower homologues of the cyclopentenyl fatty acids accompany hydnocarpic and chaulmoogric acids in some of the fats of this group; they have identified and assigned names to these as follows: $C_6H_8O_2$ (aleprolic), $C_{10}H_{16}O_2$ (aleprestic), $C_{12}H_{20}O_2$ (aleprylic), and $C_{14}H_{24}O_2$ (alepric) acids.

TABLE 55. *SEED FATS OF THE FLACOURTIACEÆ*

		Habitat	Iod. Val.	Optical Rotation $[\alpha]_D$	Chief Component Acids
Carpotroche brasiliensis	Sapocainha oil	Brazil	ca. 110	+53°	Chaulmoogric, hydnocarpic, gorlic.
Hydnocarpus Alcalæ		Philippine Islands	93	+50°	Chaulmoogric.
,, *alpina*		Ceylon	84	+49°	Chaulmoogric and hydnocarpic (oleic).
,, *anthelmintica*	Lukrabo oil	Siam	90	+51–54°	,, ,, ,,
,, *ilicifolia*		Siam, Malaya	90	+51°	,, ,, ,,
,, *Kurzii*	Chaulmoogra oil	East Indies	ca. 95	+44–51°	Chaulmoogric, hydnocarpic, gorlic, oleic.
,, *odoratus*	Gynocardia oil	East Indies, etc.	152	—	Linoleic, linolenic, oleic, etc.
,, *ovoidea*		Philippine Islands	47	+1°	Chaulmoogric, etc., apparently not present.
,, *Wightiana*	Maratti oil	East Indies	ca. 95	+54–64°	Chaulmoogric, hydnocarpic, gorlic.
Oncoba echinata	Gorli seed oil	Central Africa	98	+56°	Chaulmoogric, gorlic.
,, *spinosa*		Central Africa	177	—	Linoleic, linolenic, oleic, etc.
Pangium edule	Pitjoeng oil	East Indies, etc.	113	+4°	Oleic and linoleic; chaulmoogric, etc., if present, only in minor quantities.

COMPONENT FATTY ACIDS PER CENT. (WT.)

	Palmitic	Oleic	Lower Cyclic Homologues $C_6H_8O_2$ to $C_{14}H_{24}O_2$	Hydnocarpic $C_{16}H_{28}O_2$	Chaulmoogric $C_{18}H_{32}O_2$	Gorlic $C_{18}H_{30}O_2$
Carpotroche brasiliensis [1]	6·8	6·4	?	46·1	24·9	15·8
Hydnocarpus anthelmintica [2]	7·7	12·6	0·1	69·3	8·9	1·4
,, *(Taraktogenos) Kurzii* [2]	4·0	14·8	0·4	35·3	22·7	22·8
,, *Wightiana* [3]	1·8	6·5	3·4	48·9	27·1	12·3
Oncoba echinata [1]	7·8	2·2	?	nil	75·2	14·8

SEED FATS WITH UNSATURATED ACIDS OF THE C_{20}, C_{22}, OR HIGHER SERIES AS MAJOR COMPONENTS

The only abundant unsaturated acid of greater molecular weight than oleic acid in the vegetable kingdom is erucic (Δ^{13}-docosenoic) acid, $CH_3.[CH_2]_7.CH{:}CH.[CH_2]_{11}.COOH$, which is the main component of seed glycerides in the large and important family Cruciferæ, and which forms, apparently, a very high proportion of the component acids of the seed fats of *Tropæolum* (Tropæolaceæ). Apart from these two families, it has not been detected with certainty in any other seed fats.

In several cases, other acids have been reported, usually as minor components. Thus, in some of the Sapindaceæ seed fats (Table 57, p. 189), which contain large proportions of arachidic acid, there is evidence of the presence of small amounts of a related eicosenoic acid, $C_{20}H_{38}O_2$ [67]; whilst the unusual seed fat of *Ximenia americana* (Olacaceæ) contains in its component acids, in addition to 15 per cent. of cerotic acid, $C_{26}H_{52}O_2$, about the same proportion of a mono-ethenoid acid of the same carbon content, ximenic (Δ^{17}-*n*-hexacosenoic) acid, $C_{26}H_{50}O_2$, and a small amount of lumequic (Δ^{21}-*n*-tricosenoic) acid, $C_{30}H_{58}O_2$ (*cf.* Table 50).[68]

Finally, the lipid matter from the seeds of *Simmondsia californica*, which is unique in that it is a wax and not a fat, contains as principal acids Δ^{11}-eicosenoic, $C_{20}H_{38}O_2$, and a docosenoic acid, $C_{22}H_{42}O_2$, which is probably erucic acid. This seed wax is further discussed below (p. 185).

SEED FATS WITH ERUCIC ACID AS A MAJOR COMPONENT

Major component acids: ERUCIC, OLEIC, LINOLEIC.
Minor component acids: Palmitic, arachidic, behenic, lignoceric.

Cruciferæ seed fats. There is every reason to think that most Cruciferous plants, which form a very large family widely distributed in many parts of the world, produce seeds in which erucic acid is an important constituent. Detailed analyses have only been made so far on seed fats from four species of *Brassica* and six other genera of the family; as Table 56 (p. 184) shows, the component acids of these are all of the same general type, with about 40–50 per cent. of erucic acid as the main component.* Oleic (usually about 30 per cent.), linoleic, and occasionally linolenic, acids are also major components and account for all but about 5 per cent. of the remaining fatty acids; the latter appear to include small proportions of palmitic and still smaller, but definite, quantities of higher saturated acids (behenic or lignoceric).

Whilst the number of detailed analyses is small, and refers mainly to *Brassica* species, it should be pointed out that the high molecular weight of erucic acid results in the saponification value of fats such as those in Table 56 being about 176, whereas an oil made up entirely of glycerides of C_{18} acids has a saponification value of 190. Since the recorded saponification values of the seed oils of many other Cruciferous plants lie between 172 and 180, it is reasonable at least to conclude, pending the desirable publication of further detailed figures, that the presence in quantity of the same acid of high molecular weight (erucic) is implied.

Tropæolum seed fats. The seed fats of the nasturtium contain extremely high proportions of erucic acid. In 1899 Gadamer [69] stated that the seed

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* Except in *Hesperis matronalis*, which is rich in linolenic acid, with erucic acid absent.

Major component acids: All unsaturated—OLEIC, LINOLEIC, and ERUCIC.
Minor component acids: Linolenic, palmitic, stearic, arachidic, behenic, or lignoceric.

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.)				METHOD	OBSERVERS
			OLEIC	LINOLEIC	LINOLENIC	ERUCIC		
Brassica alba	White mustard seed	English	28	14·5	1	52·5	F	Hilditch *et al.*[1]
(*Sinapis*) *campestris*	Rape, colza seed	Indian	20·2	14·5	2·1	57·2	F	Sudborough *et al.*[2]
,, ,,	,, ,, ,,	English	32	15	1	50	F	Hilditch *et al.*[1]
,, ,,	,, ,, ,,	German	39	11	4	45	L, H	Täufel and Bauschinger.[3]
,, ,,	,, ,, ,,	East Indian	17	29	—	51	F	Hilditch and Paul.[4]
,, ,,	,, ,, ,,	,, ,,	15	16	7	54*	C, F, S	Hilditch *et al.*[15]
,, ,,	,, ,, ,,	Japanese	14	24	2	55	F, K	Yamasaki and Ichihara.[5]
,, ,,	Ravison seed	Danubian	20·5	25·5	2	47·5	F	Hilditch *et al.*[1]
,, *juncea*	Indian mustard seed	Indian	32·3	18·1	2·7	41·5	F	Sudborough *et al.*[6]
,, ,,	,, ,, ,,	,,	31	17	3	42	F	Dutt.[11]
,, *nigra*	Black mustard seed	English	24·5	19·5	2	50	F	Hilditch *et al.*[1]
Cheiranthus cheiri	Wallflower seed	Temperate zones	10	32	16	38·5	F, T	Griffiths and Hilditch.[7]
,, ,,	,, ,,	,, ,,	8	21	23	43·0	B, T	van Loon.[8]
Eruca sativa	Jamba seed	India	28·7	12·4	2·1	46·3	F	Sudborough *et al.*[9]
,, ,,	,, (rocket) seed	Germany	5·5	28·5	1	58·5	B, K	Kaufmann and Fiedler.[10]
Hesperis matronalis	Garden (Dutch) rocket	Holland	11	35	—	46	B, K	Steger and van Loon.[12a]
,, ,,	,, ,, ,,	,,	2	43	—	47	B, K	,, ,, ,, ,, [12a]
Isatis tinctoria	Woad seed	Europe	27	19	24	21	F, K	,, ,, ,, ,, [12b]
Sisymbrium-altissimum	Tumbling mustard seed	U.S.A.	5	19	35	26	F, T	Goss and Ruckman.[14]
Thlaspe arvense	Fanweed seed	,,	12·5	33	0·5	49	F	Clopton and Triebold.[13]

* Also 2·5 per cent. docosadienoic acid.

		COMPONENT FATTY ACIDS PER CENT. (WT.) SATURATED
White mustard seed	English	2 per cent. palmitic, 1 per cent. C_{20}, 1 per cent. C_{24}.
Rape seed	Indian	1·5 per cent. C_{14}, 1·6 per cent. C_{18}, 0·5 per cent. C_{22}, 2·4 per cent. C_{24}.
,, ,,	English	1 per cent. palmitic, 1 per cent. C_{24}
,, ,,	German	1 per cent. palmitic.
,, ,,	East Indian	2 per cent. palmitic, 1 per cent. C_{24}.
,, ,,	,, ,,	2 per cent. palmitic, 0·5 per cent. C_{20}, 1·5 per cent. C_{22}, 1 per cent. C_{24}.
,, ,,	Japanese	4 per cent. palmitic, 1 per cent. C_{22}.
Ravison seed	Danubian	2 per cent. palmitic, 0·5 per cent. C_{22}, 2 per cent. C_{24}
Indian mustard seed	Indian	0·5 per cent. C_{14}, 3·8 per cent. C_{22}, 1·1 per cent. C_{24}.
,, ,, ,,	,,	0·5 per cent, C_{14}, 0·5 per cent. C_{18}, 4 per cent. C_{22}, 2 per cent. C_{24}.
Black mustard seed	English	2 per cent. palmitic, 2 per cent. C_{24}.
Wallflower seed	Temperate zones	3 per cent. palmitic, 0·5 per cent. C_{24}.
,, ,,	,, ,,	5·2 per cent. (chiefly palmitic).
Jamba seed	India	4·2 per cent. C_{18}, 4·5 per cent. C_{22}, 1·8 per cent. C_{24}.
,, ,,	Germany	6·7 per cent. (palmitic, stearic, behenic).
Garden (Dutch) rocket	Holland	8 per cent. saturated
Woad seed	,,	4 per cent. palmitic, 3 per cent. stearic, 2 per cent. C_{20-24}.
Tumbling mustard seed	U.S.A.	14 per cent. palmitic.
Fanweed seed	,,	1·5 per cent. palmitic, 3·5 per cent. C_{24}.

fat of the giant nasturtium, *Tropæolum majus*, consists of nearly pure trierucin, m.p. 30·5°. This was substantially confirmed by Sudborough *et al.*[70] in 1926; these workers resolved the seed fatty acids, by the Twitchell lead salt-alcohol process (Chapter XI, p. 468), into 45·7 per cent. "solid" acids (equiv. 330, iod. val. 72·9) and 54·3 per cent. "liquid" acids (equiv. 298, iod. val. 72·6). The "solid" acids were practically entirely erucic acid, which, with subsidiary proportions of an unsaturated acid of lower molecular weight, also formed most of the "liquid" acid fraction. Their trierucin (obtained by crystallisation from the fat at 0°) melted at 30·5–31·0°; on isomerisation it gave tribrassidin, m.p. 56–57°, and on hydrogenation, tribehenin, m.p. 81·0–81·5°.

In 1938 Hilditch and Meara[71] examined the liquid fat present to the extent of 8 per cent. in the seeds of the ordinary garden nasturtium (*Tropæolum minus* or *Lobbianum* var.). The esters of the mixed fatty acids were fractionated, and the composition of the latter determined as: erucic 81·8, oleic 16·0, linoleic 1·2, and saturated acids (chiefly palmitic and behenic) 1·0 per cent. This oil also solidified on cooling to a mass of white stellate needles, which melted after recrystallisation from alcohol and benzene at 31·5–32°, and were shown by X-ray spectrographic analysis to be trierucin.

The high proportion of erucic acid in the component acids of *Tropæolum* seed fats necessitates, of course, the presence of considerable amounts of the simple triglyceride, trierucin, therein.

The liquid seed wax of *Simmondsia californica.* The seeds of this subtropical North American shrub, belonging to the family Buxaceæ (formerly placed by botanists in the Box section of the Euphorbiaceæ), are exceptional, in their botanical group, in consisting wholly of embryo and cotyledons instead of endosperm. Their lipid content is equally exceptional, indeed at present unique, in that glycerides are completely absent: it is composed of a mixture of wax esters of higher unsaturated alcohols with higher unsaturated fatty acids.

Attention was first drawn to this unusual feature by Greene and Foster,[72] who pointed out that the seed lipids were waxes and not fats (glycerides), and likened the material to the sperm oil of the sperm whale. Concurrently, but independently, the nature of the seed wax was studied later in more detail by McKinney and Jamieson,[73] and by Green, Hilditch, and Stainsby.[74] Neither group of workers could detect any glycerine in the products of hydrolysis, but both observed that the latter consisted of almost equal weights of higher aliphatic alcohols and acids. McKinney and Jamieson's fractionation figures led to the following percentage compositions for the alcohols and acids: *Alcohols*—eicosenol, $C_{20}H_{39}.OH$, 30 per cent.; docosenol, $C_{22}H_{43}.OH$, 70 per cent.; *Acids*—saturated 3·5, hexadecenoic 0·5, oleic 1·4, eicosenoic 64·4, and docosenoic 30·2 per cent. Green, Hilditch, and Stainsby's fractionation data are in general agreement with these, but were not employed for quantitative calculation; the saturated acid present appeared to be mainly palmitic acid. By disruptive oxidation, and by hydrogenation of the respective individual acids and alcohols to the corresponding saturated derivatives (which were submitted to X-ray spectrographic analysis), they established the structure of the alcohols as *n*-Δ^{11}-eicosenol and *n*-Δ^{13}-docosenol, and that of the main acid component as *n*-Δ^{11}-eicosenoic acid; it is almost certain that the higher acid is Δ^{13}-docosenoic (erucic) acid.

(*b*) SEED FATS CONTAINING SPECIFIC SATURATED ACIDS

As in the case of the rarer unsaturated acids of vegetable origin which have just been discussed, the occurrence of saturated acids other than palmitic in quantity is of a very specific nature and is confined, broadly speaking, to the seed fats of members of the following families :

Specific Saturated Major Components	Families
Arachidic (behenic, lignoceric)	Leguminosæ, Sapindaceæ.
Stearic	Meliaceæ, Sterculiaceæ, Guttiferæ, Dipterocarpaceæ, Sapotaceæ.
Myristic	Myristicaceæ (Vochysiaceæ)
Lauric	Lauraceæ.
Lauric and myristic (together)	Palmæ, Simarubaceæ (Salvadoraceæ).

Seed Fats of which Arachidic (Behenic) or Lignoceric Acids are Major Components

Major component acids: OLEIC, LINOLEIC, ARACHIDIC, (BEHENIC), LIGNOCERIC.

Minor component acids: Palmitic, stearic, (myristic, arachidic, lignoceric, linolenic).

The data in existence at present for this group are collected in Table 57 (pp. 188, 189).

Leguminosæ seed fats. The data for these are interesting from several points of view, and suggest that this family (perhaps especially its subdivision Mimosoideæ) may prove a very interesting field for further investigation of the component acids of seed fats. The *Pentaclethra* fats are reported to be rich in arachidic acid and fresh and more rigorous analyses of the saturated acid components are clearly desirable. The *Adenanthera* fat has been fully investigated by workers at the Indian Institute of Science, Bangalore, and the presence of 25 per cent. of lignoceric (*n*-tetracosanoic) acid is unequivocally established. An analysis of *Parkia* seed fat seems to indicate equally definitely the occurrence of behenic (*n*-docosanoic) acid in this case, although to a less extent ; behenic acid is also prominent in the seed fat of *Xylia xylocarpa*. On the other hand, the saturated acids of seed fats of *Acacia* species from the Sudan and of *Albizzi lebbek* (India) are stated by Grindley [119] to be principally palmitic acid, but to include 2 to 4 per cent. of mixtures of arachidic, behenic, and lignoceric acids :

	Saturated	C_{20-24}	Oleic	Linoleic
Acacia albida	22	2·2	45	33
A. arabica	22	1·2	42	36
A. mellifera	35	4·4	43	22
A. seyal	26	2·9	36	38
A. sieberiana	25	4·4	31	44
A. verek	24	3·1	38	38
Albizzi lebbek	29	3·1	43	28

In the other botanical sub-divisions (Cæsalpinioidæ and Papilionatæ) no striking instance of large proportions of arachidic or higher saturated acid has yet been encountered. There seem here to be, however, two types of seed fat component acid mixtures with no sharply defined boundary between them. In one group the saturated C_{20}, C_{22}, and/or C_{24} acids are present, albeit as minor components in these cases ; together they may amount to nearly 15 per cent. of the total acids (as in tonka bean oil) or to 6–7 per cent.

(as in groundnut and pongamia oils). In this type of seed fat there is also usually 5–8 per cent. of palmitic and a smaller amount of stearic acid. In the other group, whilst the palmitic and stearic acid contents are usually similar to those just mentioned, the amount of higher saturated acids is almost negligible and is, as a matter of fact, no higher than has frequently been noted as arachidic or lignoceric acid in many of the liquid fats discussed in Tables 49, 50, 51, and 52.

It should be observed that, in one important respect, all the Leguminosæ seed fats resemble the simple " linoleic-oleic-palmitic " type dealt with in detail in Table 50 : the chief components are oleic and linoleic acids, these together usually forming 60–80 per cent. of the total component acids. Linolenic acid is often present in small proportions (e.g. especially, soya bean oil), but rarely in quantity, although it forms over 20 per cent. of the component acids of alfalfa seed fat. Possibly the clovers, lucernes, and other small leguminous herbs elaborate more linolenic acid than some of the larger species, but more data are necessary to illustrate this point. In different species in Table 57, the linoleic acid content may greatly exceed the oleic acid content, or *vice versa.* It is not yet possible to correlate these variations with biological variations or with differences in temperature, although the former may at present appear on the whole more likely.

Cooler temperatures of growth might be considered to account for the high linoleic/oleic acid ratio in Spanish and Virginian groundnuts as compared with West African groundnuts, or for the higher linoleic/oleic acid ratio as between groundnuts on the one hand, and soya beans on the other. Contrariwise, the linoleic/oleic acid ratio is higher in the tropical Bonducella nut than in the sub-tropical soya bean or the Manchurian mungo bean.

Groundnut and soya bean oils. Results of a number of studies of oils from groundnuts and soya beans grown under controlled conditions have been published, and serve to supplement the data quoted in Table 57.

In the case of *groundnuts,* selected varieties or hybrids grown experimentally in Georgia, U.S.A. yielded oils [110] with the component acids shown below. For comparison, the chief data in Table 57 are again quoted here in order to emphasise what was stated in the preceding paragraph as regards the possible connection in groundnut oils between climatic temperature and the linoleic/oleic acid ratio.

GROUNDNUT OILS	COMPONENT FATTY ACIDS			METHOD
SOURCE	SATURATED	OLEIC	LINOLEIC	
Philippine	18	55	27	F
Spanish	18	56	26	,,
,,	22	53	25	,,
Senegal	15	66	19	,,
W. Africa	18	60	22	,,
,,	18	65	17	,,
Virginia	17	61	22	,,
Georgia :—				
var. N. C. Runner	20	53	27	T
,, Improved W. Spanish	23	45	32	,,
Hyb. Spanish × Basse	23	50	27	,,
,, Basse × Dixie Giant	18	60	22	,,

There appear to be two main types of groundnut oil, differing slightly as follows in their component acids :

SATURATED	OLEIC	LINOLEIC
15–18	66–60	19–22
18–23	56–50	25–27

TABLE 57. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS OF THE LEGUMINOSÆ AND SAPINDACEÆ*

Major component acids: OLEIC, (ARACHIDIC, BEHENIC, LIGNOCERIC, LINOLEIC).
Minor component acids: Palmitic, stearic, (myristic, arachidic, lignoceric, linolenic).

		Habitat	Component Fatty Acids Per Cent. (Wt.)							Method	Observers
			Saturated					Oleic	Linoleic		
			C_{16}	C_{18}	C_{20}	C_{22}	C_{24}				
LEGUMINOSÆ											
Sub-family *Mimosoideæ* (see also *Acacia* sp., p. 186).											
Adenanthera pavonina	Coral tree nut	India	9·0(*a*)	1·1	—	—	25·5	49·3	14·7	F, H	Mudbidri *et al.*[1]
Parkia biglandulosa	Parkia seed	,,	8·8	13·3	—	7·9	—	30·6	39·4	F, H	Paranjpe.[2]
Pentaclethra filamentosa	Paroacaxy nut	Brazil	← ca. 28 →		← ca. 25 →			← ca. 47 →		?	Margaillan *et al.*[3]
,, *macrophylla*	Owala nut	W. Africa	← ca. 30 (? chiefly C_{20}) →					← ca. 70 →		?	Margaillan *et al.*[3]
,, ,,	,, ,,	,,	← 34 (C_{18} and C_{24}) →					← 66 →		L	Denis.[4]
Xylia xylocarpa	—	India	Trace	Trace	—	17·3	Some	67·5	12·5		Manjunath and Nagaraj.[30]
Sub-family *Cæsalpinioidæ*											
Bauhinia variegata	Kachnar seed	,,	17 (*q*)	13·4	—	—	1	31·8	35·8	L, F	Puntambekar and Krishna.[31]
Cæsalpinia Bonducella	Bonducella nut	Tropics	10	6	—	—	—	22	62	L, H	Godbole *et al.*[5]
Cassia absus			7·8	10·1	—	—	1·0	20·4	59·2(*b*)	F, H	Ahmad.[6]
,, *occidentalis*	Wild coffee seed		←22·5→		—	—	—	34	37(*c*)	B, T	Steger and van Loon.[7]
Sub-family *Papilionatæ*											
†*Arachis hypogæa*	Ground-nut	Virginian	6·3	4·9	← 5·9 →			61·1	21·8	F, H	Jamieson *et al.*[8]
,, ,,	,,	Spanish *	8·3	6·3	← 7·1 →			53·4	24·9	F, H	Jamieson *et al.*[8]
,, ,,	,,	Indian (?) *	9·4 (*r*)	3·1	—	5·1	—	54·9	26·2	F	Longenecker.[32]
,, ,,	,,	,, (?) *	8·3	3·1	2·4	3·1	1·1	56·0	26·0	F	Jasperson *et al.*[9]
,, ,,	,,	,, (?) *	8·0 (*v*)	4·4	← 6·6 →			52·5	26·3	C, F	Hilditch and Riley.[39]
,, ,,	,,	Argentine *	11·4 (*w*)	2·8	← 7·3 →			42·3	33·4	C, F	Hilditch and Riley.[39]
,, ,,	,,	Philippine	8·6	3·6	← 5·9 →			54·5	27·4	F	Cruz and West.[10]
,, ,,	,,	Senegal	7·3	2·6	← 5·2 →			65·7	19·2	F	Armstrong and Allan.[11]
,, ,,	,,	W. Africa	6·0	3·0	← 6·5 →			71·5	13·0	F	Hilditch and Vidyarthi.[12]
,, ,,	,,	,,	8·2	3·4	← 6·1 →			60·4	21·9	F	Griffiths *et al.*[13]
,, ,,	,,	,, *	8·7	3·1	← 6·6 →			64·8	16·8	F	Jasperson.[14]
Dipteryx odorata	Tonka bean	Malaya (expressed)	5·1	5·9	← 14·8 →			61·0	13·2	F	Hilditch and Stainsby.[15]
,, ,,	,,	,, (extracted)	6·1	5·7	← 13·2 →			59·6	15·4	F	Hilditch and Stainsby.[15]
Erythrina christogalli	—	Argentine	11·4 (*x*)	3·9	3·2	—	—	50·9	18·9	F	Cattaneo.[41]
Galega officinalis	Lagwort	Europe	20	25	—	—	—	9	46	L, H	Fink and Richter.[33]
Medicago sativa	Alfalfa seed	U.S.A.	← 10·3 →					7	71(*d*)	L, T	Schuette *et al.*[16]
,, ,,	,, ,,	Switzerland	9·5	4·7	—	—	—	11	43(*s*)	F, T	Hilditch and Zaky.[34]
Pachyrhizus angulatus	Seed	India	← 38 →					34	28	L	Nag, Banerjee and Pain.[17]
Phaseolus Mungo	Mungo bean	Manchuria	28	8	3	—	—	18	40(*e*)	?	Miki and Sera.[18]
Pongamia glabra	Hongay seed	E. Indies	6·6(*f*)	2·4	4·7	—	3·5	71·3	10·8	F, H	Desai *et al.*[19]
,, *pinnata*	,, ,,	Philippine Is.	← 23 →					11	66	L	Soliven.[20]

Psoralea drupacea		Asia	← 9 →		—	—	—	← 91 →		L	Tsukervanik and Bersutski.[21]
†*Soja hispida*	Soya bean	Manchuria	6·8	4·4	0·7	—	0·1	34	52(*g*)	F, H	Baughman and Jamieson.[22]
,, ,,	,, ,,	Japan	← 12 →		—	—	—	22	66	L, T	Kimura.[23]
,, ,,	,, ,,	Manchuria	14	—	—	—	—	26	57(*i*)	L, H	Heiduschka and Eger.[24]
,, ,,	,, ,,	,,	7·0	5·5	0·3	—	—	23	60(*j*)	F, T	Griffiths *et al.*[13]
,, ,,	,, ,,	Philippines	9·0	3·9	0·6	—	—	30·5	54(*k*)	F, H	Cruz and West.[25]
,, ,,	,, ,,	Asia.*	9·8	2·4	0·9	—	—	25·5	58(*l*)	F, T	Jasperson.[26]
Trigonella fœnum græcum	Fenugreek seed	U.S.A.	8·4	2·7	1·0	0·7	—	11	70(*t*)	F, T	Schuette *et al.*[35]
Vicia faba	Horse bean	Canada	← 7·5 →					57·5	35	T	Labarre and Pfeffer.[42]
MORINGACEÆ											
Moringa oleifera	Ben seed	Haiti	3·9(*u*)	11·5	—	6·6	0·2	72·2	4·0	F	Jamieson.[36]
,, ,,	,, ,,	Trinidad	5·4	7·8	← 9·2 →			75·9 (*y*)	0·8	C, F, S	Dunn and Hilditch.[40]
OCHNACEÆ											
Lophira alata	Oyster, Niam seed	W. Africa	27·1(*h*)	—	—	14·2	2·3	14·5	33·3	F	Hilditch and Meara.[37]
SAPINDACEÆ											
Nephelium lappaceum	Rambutan tallow	Malaya	2·0	13·8	34·7	—	—	45·3	—(*m*)	F	Hilditch and Stainsby.[15]
,, *mutabile*	Pulasan tallow	,,	3·0	31·0	22·3	—	—	43·7	—	F	Hilditch and Stainsby.[15]
Sapindus Drummondii	Western soapberry	Oklahoma	← 23 →					57	20	L, T	Dermer and Crews.[38]
,, *trifoliatus*	Soap nut	India	5·6	8·5	21·9	—	2·5	61·5	—	F, H	Paranjpe and Ayyar.[27]
Schleichera trijuga	Kusum, macassar nut	,,	5·3(*n*)	6·3	19·8	—	3·5	61·6	2·5	F, H	Dhingra *et al.*[28]
,, ,,	,, ,, ,,	,,	8·7(*o*)	1·7	22·6	—	2·2	59·2	4·5	F, H	Dhingra *et al.*[28]
,, ,,	,, ,, ,,	,,	7·9(*p*)	—	31·1	—	—	57·6	—		Patel.[29]

(*a*) Also 0·4 per cent. myristic acid.
(*b*) Also 1·0 per cent. hydroxy acids and 0·5 per cent. linolenic acid.
(*c*) Also 6·5 per cent. linolenic acid.
(*d*) Also 11 per cent. linolenic acid.
(*e*) Also 3 per cent. linolenic acid.
(*f*) Also 0·2 per cent. myristic and 0·5 per cent. linolenic acids.
(*g*) Also 2 per cent. linolenic acid.
(*h*) Also 1·9 per cent. myristic, 1·5 per cent. hexadecenoic, and 5·2 per cent. docosenoic acids.
(*i*) Also 3 per cent. linolenic acid.
(*j*) Also 3 per cent. linolenic acid.
(*k*) Also 2 per cent. linolenic acid.
(*l*) Also 0·3 per cent. myristic or lower saturated, 0·1 per cent. tetradecenoic, 0·4 per cent. hexadecenoic, and 3 per cent. linolenic acid (full analysis for minor components, carried out on 1,140 g. of mixed fatty acids).
(*m*) Also 4·2 per cent. eicosenoic acid, $C_{20}H_{38}O_2$.
(*n*) Also 1·0 per cent. myristic acid.
(*o*) Also 1·1 per cent. myristic acid.
(*p*) Also 1·1 per cent. decanoic and 2·3 per cent. lauric acids.
(*q*) Also 1 per cent. myristic acid.
(*r*) Also 0·4 per cent. myristic and 0·9 per cent. hexadecenoic acids.
(*s*) Also 32 per cent. linolenic acid.
(*t*) Also 6 per cent. linolenic acid.
(*u*) Also 1·6 per cent. myristic acid.
(*v*) Also 0·5 per cent. myristic and 1·7 per cent. hexadecenoic acids.
(*w*) Also 0·4 per cent. myristic and 2·4 per cent. hexadecenoic acids.
(*x*) Also traces C_{10}, C_{12}, 1·9 per cent. myristic and 9·0 per cent. eicosenoic acids.
(*y*) Also 0·9 per cent. hexadecenoic acid.

* In these analyses the presence of traces of hexadecenoic acid was also verified.
† See also in text for *groundnut* and *soya bean oils* (pp. 187, 190).

More evidence is available for *soya bean oils*, a number of controlled studies of these having been made in recent years in the United States. In 1933, Jamieson, Baughman and McKinney[111] gave the characteristics of soya bean oils from different varieties of seed grown in various localities of the United States suitable for soya bean culture. The component acids in the oils, calculated from lead salt separation (L) and iodine and thiocyanogen values (T), were :

VARIETY	OIL	COMPONENT FATTY ACIDS			
	I.V.	SAT.	OL.	LIN.	LEN.
Dunfield	131·4	13·5	32	44·5	10
Manchu	131·0	13	29	52	6
Haberlandt	131·0	13·5	28·5	51	7
Virginia	127·8	13·5	31·5	49	6
Chiquita	140·7	13	25	49	13
Mammoth Yellow	129·4	13	33	46	8

In 1938, Dollear, Krauczunas and Markley [112a] published figures for three oils from seeds of the Dunfield variety grown in Missouri and Indiana, one of which, grown in Missouri in a very abnormal (hot and dry) season in 1936, yielded an oil of exceptionally low iodine value. In 1940 the same workers [112b] gave similar data for four other varieties grown in Illinois and in New York State. They concluded that the abnormally low unsaturation of the 1936 Missouri crop was due to a combination of factors—varietal, climatic and soil ; and that, although the relative influence of each environmental factor cannot be evaluated, the total effect produced in this instance a considerable lowering of the total unsaturation. These authors have further pointed out that, as the total unsaturation of the oils varies, the proportions of saturated acids remain remarkably constant, whilst those of linolenic and linoleic acids increase more or less regularly with increasing iodine values of the oils, and those of oleic acid at the same time decrease progressively. These findings are borne out not only by their own figures, but by the other data recorded here and in Table 57. The figures obtained by Dollear *et al.* (in which the saturated acids were determined by lead salt separation (L), and the unsaturated acids by thiocyanometric (T) analysis) are as follows :

VARIETY	GROWN IN	OIL	COMPONENT FATTY ACIDS			
		I.V.	SAT.	OL.	LIN.	LEN.
Dunfield	Missouri, 1936	102·9	12	59	28	1
,,	,, 1937	124·0	13	33·5	50·5	3
,,	Indiana, 1937	127·3	13	31	53	3
Illini	Illinois, 1936	131·6	13	27	56	4
Peking	,, 1937	137·8	12	22	61	5
Seneca	New York, 1938	139·4	12	23	59	6
Wild beans	Illinois, 1938	151·4	13	10	66	10

Similar conclusions, based upon analyses of 95 specimens of soya bean oil of iodine values ranging from 99·6 to 147·6, were recorded by Scholfield and Bull[120] in 1944.

Finally, the component acids of three soya bean oils of unspecified origin analysed by Mitchell, Kraybill and Zscheile [95] both by thiocyanometric (T) and spectrographic (S) methods may be added here :

SOYA BEAN OIL	I.V.	COMPONENT FATTY ACIDS				METHOD
		SAT.	OL.	LIN.	LEN.	
1	136·5	14	23	54	9	T
1	,,	15	22	53	10	S
2	134·3	14·5	24	53·5	8	T
2	,,	15	23	55	7	S
3	130·0	15	27	52	6	T
3	,,	17	22	56	5	S

A word should be added here with reference to the small amounts of arachidic, behenic, and lignoceric acids which make up 6–7 per cent. of the component acids of *Arachis*, *Pongamia*, and perhaps other leguminous seed oils. In these cases the small amounts of each acid present render complete separation of the individuals very difficult, and much discussion (*cf.* Chapter IX, p. 393) has taken place as to their identity, since in many instances neither the melting points nor the X-ray spectra of the isolated acids agreed with those of *n*-eicosanoic or *n*-tetracosanoic acids. Several investigators of this problem concluded that the arachidic acid of groundnut oil, for example, was a branched-chain acid and thus an exception to the otherwise invariable rule that natural fatty acids contain an unbranched chain of carbon atoms. The most recent work on the matter, however, is due to Jantzen and Tiedcke,[75] who succeeded in effecting the separation of the methyl esters of the mixed higher saturated acids of groundnut oil by means of a special form of distillation apparatus, and who then obtained definite fractions of *n*-eicosanoic, *n*-docosanoic, and *n*-tetracosanoic acids. In view of this, it seems probable that the difficulties encountered in correlating particular physical properties of the synthetic and natural arachidic, etc., acids were due in some way to the influence of small amounts of another component contaminating a supposedly individual acid. At all events, since the normal arachidic, lignoceric, and behenic acids have now been reported as major components of one or other leguminous seed fat, it seems reasonable to anticipate that the higher saturated acids occurring as minor components of certain other seed fats in this family should also be mixtures of the same (straight-chain) acids.

Sapindaceæ seed fats. The four seed fats of this family which have been examined in detail were found each to contain 20 per cent. or more of arachidic acid. It seems likely, therefore, that arachidic acid is elaborated in quantity in the seeds of the tropical trees and shrubs belonging to this botanical group. In view of the discussion which has taken place (*cf.* above and Chapter IX, p. 393) with regard to the identity of the arachidic and lignoceric acids of groundnut oil, it is of interest to mention that specimens of the arachidic acid from the seeds of *Schleichera trijuga* and of *Nephelium lappaceum* have been submitted to X-ray spectrographic analysis, and in each case the X-ray spectra corresponded exactly with that of *n*-eicosanoic acid, $CH_3.[CH_2]_{18}.COOH$.

It is worthy of record that the 35 per cent. of arachidic acid in the seed fat of *Nephelium lappaceum* was accompanied by about 4 per cent. of an eicosenoic acid, $C_{20}H_{38}O_2$, and that traces of the latter acid were apparently present in the component acids of the seed fat of *N. mutabile*, of which arachidic acid amounted to 22 per cent.

The occurrence of behenic acid, noted in some quantity in the seed fats of two species, belonging in one case to the family Moringaceæ and in the other to Ochnaceæ, raises the possibility that there may be here another instance of a saturated acid—in this instance behenic acid, $C_{22}H_{44}O_2$—specific to the seeds of plants of the families in question.

SEED FATS OF WHICH STEARIC ACID IS A MAJOR COMPONENT

Major component acids: OLEIC, STEARIC, PALMITIC.
Minor component acids: Linoleic, (myristic, arachidic).

It was remarked on p. 176, in connection with Table 52, that as seed fats become less unsaturated, and palmitic acid makes its appearance in larger quantities, so in some instances there is also an increase in stearic acid content. We come now to a group of families in which stearic acid is nearly always present, in the seed fats, to the extent of over 10 per cent.; in some cases it becomes the chief component and forms over 50 per cent. of the mixed fatty acids of the glycerides. Its occurrence in quantity in seed fats has, however, only been observed in plants belonging to a few tropical families, and it cannot be too much emphasised that, in the vegetable kingdom, stearic acid is at least as rare as, for example, arachidic or elæostearic acid, and is probably produced in less abundance than lauric, erucic or petroselinic acids, the respective characteristic components of the very large and widely distributed natural families Palmæ, Cruciferæ, and Umbelliferæ.

There was some indication in the "drying" and "semi-drying" oils dealt with in Tables 49 and 50 (pp. 154–165) that the relative amounts of oleic, linoleic, and linolenic acid in seed fats of related species alter in some measure correspondingly; that is to say, one does not often find cases in which a seed fat contains much oleic and linolenic with little linoleic acid. Progressive development of unsaturation from a "non-drying" to a "drying" oil is usually regular, in the sense that oleic acid content falls somewhat as the amount of linoleic acid increases, and may be still more reduced in cases where linolenic acid makes its appearance. This is suggestive, of course, of some kind of inter-relation between the three unsaturated acids or their immediate precursors in the endosperm metabolism, but no rigorous proof has yet been offered of the direct conversion, for example, of oleic into linoleic acid, or *vice versa*, in the seed. Whilst such interconversion may or may not occur between the three unsaturated acids, it is, nevertheless, in the writer's opinion, most unlikely that any such process accounts for the appearance, in the fats under notice at the moment, of large amounts of stearic acid; for, were this the case, we should expect stearic acid to be at least as prominent a feature as palmitic acid of those oils in which the latter is only a minor component. The facts point in exactly the opposite direction; palmitic acid most frequently forms at least 6–10 per cent. of the less saturated seed fats and sometimes more, whilst (except in a very few families) the proportion of stearic acid is very small (often 1–2 per cent. or less) and not seldom it is completely absent. It appears more logical, therefore, for the time being to regard stearic acid, when present as a major component of seed fats, on the same footing as arachidic, lauric, erucic, petroselinic, and other "specific" acids.

The above argument, of course, is intended to apply only to the stearic acid of vegetable fats. We saw that in the case of animal reserve fats (Chapter III, pp. 90, 96) there is a very different state of affairs, and that there is strong evidence of a very close inter-connection between the stearic and oleic acid content of such fats.

It will be observed that, even within the limits of a single family, there are various proportions in which stearic and palmitic acids are found. For example, there are several cases (e.g. *Azadirachta indica*, *Calophyllum inophyllum*, or *Calocarpum mammosum* fats) in which the palmitic content is of the order of about 10 per cent. and the stearic content only 20 per cent. or even less; in another group (e.g. *Theobroma cacao* and *Shorea aptera*) the stearic content reaches 35–40 per cent. and the palmitic content also rises to somewhat over 20 per cent.; whilst there is a third category marked by extremely high proportions of stearic acid (50 per cent. or thereabouts) with very small amounts of palmitic acid.

More often than not, linoleic acid is only present in quantity in cases where stearic acid forms 20 per cent. or less of the total acids ; but, as indicated above, the writer prefers to regard this as an instance of the usual state of things that, when the total proportion of saturated acids is relatively small and of unsaturated acids relatively great, the latter generally includes appreciable amounts of linoleic as well as oleic acid. The disappearance of linoleic acid when conditions are reversed, and saturated acids preponderate in the whole fat, is no more likely to connote conversion of linoleic into stearic acid in *Allanblackia* or *Shorea* seed fats than, for example, its conversion on similar but unlikely lines into lauric or myristic acids in those of *Cocos*, *Elæis*, or *Myristica* species (*cf.* Table 59A and 59B).

Fats which are made up almost exclusively of stearic and oleic acids, with the former often predominating, are confined (according to the existing records) to seeds of certain genera of the Guttiferæ and Sapotaceæ. In addition to those for which quantitative data are given in Table 58 (pp. 194–196) the following seed fats have also been stated to contain stearic acid as the chief saturated component acid, although definite figures are not given :

	GUTTIFERÆ	
Pentadesma Kerstingii		Pacific Is.
Platonia insignis		S. America.
Symphonia fasciculata	Hazina kernel	Madagascar.
,, *globulifera*	Mani nut	Tropics.
,, *lævis*		Madagascar.
	SAPOTACEÆ	
Payena oleifera	Kansive nut	Burma.

It is interesting to note, as pointed out earlier (p. 155), that the tropical gymnosperm *Gnetum scandens* produces a seed fat containing 56 per cent. of stearic acid and 14 per cent. of palmitic acid, thus possessing marked resemblances to the stearic-rich seed fats of the Sapotaceæ and Guttiferæ families.

It is to be hoped that further additions will be made to our knowledge of the proportions of the component acids in this interesting group of seed fats. The presence of large amounts of stearic (and sometimes also palmitic) acid, and the fact that oleic acid is practically the only other component, not only renders the fatty acid composition of interest, but also makes fats of this type especially suitable for the investigation of glyceride structure (*cf.* Chapter VI).

Perusal of Table 58 suggests that, whilst within any of the families there may be considerable variation in the proportions of oleic, stearic, and palmitic acids in the seed fats, there is a general tendency towards the following relations :

Guttiferæ and Sapotaceæ seed fats : Rich in stearic and oleic ; little palmitic and linoleic.

Dipterocarpaceæ and Burseraceæ seed fats : Rich in stearic and oleic, but also in palmitic acid, the latter frequently about 20 per cent. of the total acids ; linoleic acid almost absent.

Meliaceæ, Convolvulaceæ, and Verbenaceæ seed fats : Less rich in stearic, which is, however, still prominent ; moderate proportions of palmitic acid ;

TABLE 58. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS (USUALLY RICH IN STEARIC ACID)*

Major component acids: OLEIC, STEARIC, PALMITIC.
Minor component acids: Linoleic, (myristic, arachidic).

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.)				METHOD	OBSERVERS
			PALMITIC	STEARIC	OLEIC	LINOLEIC		
GYMNOSPERM								
GNETACEÆ								
Gnetum scandens		India	14	56	27	3	L	Varier.[58]
ANGIOSPERMS								
MELIACEÆ								
Amoora Rohituka	Amoora seed	India, Africa	7·8	15·1	11·2	57·4(*a*)	F, H	Ayyar and Patwardhan.[1]
Azadirachta indica	Neem, margosa seed	India	14·1(*b*)	24·0	58·5	—	?	Roy and Dutt.[2]
,, ,,	,, ,, ,,	Ceylon	13·6	19·1(*c*)	49·1	15·8	F	Child and Ramanathan.[3]
,, ,,	,, ,, ,,	India	14·9	14·4(*d*)	61·9	7·5	F	Hilditch and Murti.[4]
,, ,,	,, ,, ,,	,,	13·8	18·2(*a′*)	52·6	13·6	F	Rao and Seshadri.[44]
Carapa guyanensis	Andiroba seed	S. America	13·3(*b′*)	—	62·4	5·2	?	de Amorin.[45]
Trichilia emetica		Sudan	←——54——→		43	3	L, T	Henry and Grindley.[46]
STERCULIACEÆ								
Brachychiton diversifolium		?	8·5	6·1	72·7	12·7	L	Labruto and de Angelis.[47]
Sterculia fœtida	Java olive	E. Indies	(Major component acid C_{19} series: see text, p. 197)				F	Hilditch, Meara and Zaky[48]
,, *parviflora*		,,					L	Hilditch and Meara.[48]
,, *platonifolia*		Japan (?)	←——25——→		45	30	?	Ueno and Ueda.[5]
,, *tomentosa*		Sudan	←——22——→		46	32	L, T	Henry and Grindley.[46]
Theobroma cacao	Cacao butter	Tropics	24·4	34·5	39·1	2·0	F	Lea.[6]
,, ,,	,, ,,	,,	24·4	35·4	38·1	2·1	F	Hilditch and Stainsby.[7]
	Cotyledons	,,	←— 60 to 66 —→		36 to 30	3·5 to 4	B, T	Bauer and Seber.[8]
,, ,,	Embryo	,,	←— 41 to 49 —→		23 to 28	36 to 23	B, T	,, ,,
	Seed shells	,,	←— 51 to 56 —→		33 to 35	16 to 9	B, T	,,
GUTTIFERÆ								
Allanblackia floribunda	Bouandja	Nigeria	—	52–56	48–44	—	L	Pieraerts and Adriaens.[9]
,, ,,	,,	,,	2·1	57·1(*e*)	38·7	1·4	F	Bushell.[10]
,, ,,	,,	,,	2·9	57·1(*c′*)	39·4	0·4	F	Meara and Zaky.[12]
,, *klainei*		W. Africa	—	62·5	37·5	—	?	Adriaens.[11]
,, *parviflora*		Gold Coast	3·5	52·7	43·8	—	F	Meara and Zaky.[12]
,, *Sacleuxii*	Kagné	Africa	—	ca. 82 (?)	ca. 18 (?)	—	?	Jumelle.[13]
,, *Stuhlmannii*	Mkanyi	E. Africa	—	ca. 55	ca. 45	—	L	Heise.[14]
,, ,,	,,	,,	3·1	52·6	44·1	0·2	F	Hilditch and Saletore.[15]
Calophyllum inophyllum	Indian laurel kernel	India	16·8	9·7	49·7	23·8	F	Dhingra and Hilditch.[16]
,, ,,	Dilo kernel	Fiji	15·6	12·2	53·1	15·8(*f*)	F	Glasgow.[17]

Garcinia Cambŏgia	Gamboge butter	India	—	30 (?)	70 (?)	—	?	Rau and Simonsen.[18]
,, *echinocarpa*	Madol nut	Ceylon, S. India	3·7	43·7	52·6	—	L	Child.[49]
,, *indica*	Kokum butter	India	2·5	56·4	39·4	1·7	F	Hilditch and Murti.[19]
,, ,,	,, ,,	,,	5·3(*d′*)	52·0	41·5	—	F	Vidyarthi and Rao.[50]
,, *morella*	Gurgi nut	,,	7·2(*g*)	42·5	43·6	6·1	F	Dhingra *et al.*[20]
,, ,,	,, ,,	,,	0·7	46·4(*h*)	49·5	0·9	F	Hilditch and Murti.[19]
Mesua ferrea	Iron wood nut	Bengal	8·5(*i*)	10·4	66·5	11·2	F	Dhingra and Hilditch.[16]
,, ,,	,, ,, ,,	Malabar	8·4(*j*)	14·2	65·4	9·7	F	Dhingra and Hilditch.[16]
,, ,,	,, ,, ,,	India	8·2	15·8(*k*)	55·4	19·6	?	Chatterji and Gupta.[21]
Pentadesma butyracea	Kanya butter	W. Africa	5·4	46·1	48·5	—	F	Hilditch and Saletore.[15]
,, ,,	,, ,,	E. Indies	7·7	39·7	49·0	1·6	B	Frahm.[51]
DIPTEROCARPACEÆ								
Shorea stenoptera	Borneo tallow	Malaya, Borneo	21·5(*l*)	39·0	38·1	—	F	Hilditch and Priestman.[22]
,, ,,	,, ,,	,, ,,	18·0	43·3(*m*)	37·4	0·2	F	Bushell and Hilditch.[23]
,, *robusta*		N. India	4·5	44·2(*e′*)	42·2	2·8	F	Hilditch and Zaky.[52]
Vateria indica	Dhupa, Malabar tallow	S. India	10·2	38·9(*n*)	47·8	—	F	Hilditch and Jones.[24]
,, ,,	,, ,, ,,	,,	13·0(*f′*)	43·1	42·5	0·1	F	Venkatarao and Narasingarao.[53]
BURSERACEÆ								
Canarium commune	Java almond	E. Indies	29·5	15	43	12·5	L, H	Pastrovich.[59a]
,, ,,	Canari seed (expressed)	,,	29·0	9·7	38·3	21·8(*i′*)	F	Steger and van Loon.[59b]
,, ,,	,, ,, (extracted)	,,	30·5	10·2	39·9	18·7(*j′*)	F	,, ,,
,, *ovatum* ,, syn. *pachyphyllum*	Pili nut	Philippine Is.	38·2	1·8	60	—	F	West and Balce.[54]
Dacryodes rostrata	Java almond	Borneo	10·7	40·3(*o*)	43·6	3·3	F	Hilditch and Stainsby.[25a]
,, ,,	,, ,,	Malaya	12·7(*k′*)	30·9	49·5	2·8	F	Hilditch, Meara and Zaky.[25b]
SAPOTACEÆ								
Acharas sapota	Sapota seed	India	12·6(*g′*)	12·0	66·2	1·4	F	Vidyarthi and Mallya.[55]
Autranella congolensis		Belgian Congo	←— 22 —→		78	—	?	Adriaens.[26]
Butyrospermum Parkii	Shea butter	W. Africa	8·5(*p*)	35·9	49·9	5·3	F	Hilditch and Saletore.[15]
,, ,,	,, ,,	,,	5·7	41·0	49·0	4·3	F	Green and Hilditch.[27]
Calocarpum mammosum	Mammy apple	Honduras	10·0	22·3	54·3	13·4	F	Jamieson and McKinney.[28]
Dumoria Africana		W. Africa	—	46	54	—	L	Pieraerts *et al.*[29]
Madhuca † *butyracea*	Phulwara butter	India	54	—	46	—	L, H	Pelly.[30]
,, ,,	,, ,,	,,	56·6	3·6	36·0	3·8	F	Bushell and Hilditch.[31]
,, *latifolia*	Mowrah butter	Bengal	←— 34 —→		66	—	L, H	Pelly.[30]
,, ,,	,, ,,	India	27·1(*q*)	2·0	41·0	13·6	F	Gill and Shah.[32]
,, ,,	,, ,,	,,	16·0(*r*)	25·1	45·2	9·4	F	Dhingra *et al.*[20]
,, ,,	,, ,,	,,	23·7	19·3	43·3	13·7	F	Hilditch and Ichaporia.[33]
,, *longifolia*	Illipé butter, Mee oil	India, Ceylon	←— 40 —→		51	9	L, H	Pelly.[30]
,, ,,	,, ,, ,, ,,	,, ,,	28·2	14·1	48·8	8·9	F	Child and Hilditch.[34]
,, *Mottleyana*	Katio kernel	Borneo	10	18·5	69	2·5	L	Zimmermann.[35]
Mimusops elangi	—	India	11·0	10·1 (*l′*)	64·0	14·5	F	Kartha and Menon.[60]
,, *hexandra*	Rayan seed	N. India	19	14(*s*)	63	3	L	Patel.[36]
,, *Heckelii*	Dumori butter	W. Africa	4·2	35·5(*t*)	58·5	Trace	F	Atherton and Meara.[37]
,, *Njave*	Njave, Baku butter	,,	4·4	36·0(*h′*)	58·5	0·3	F	,, ,, [37]

TABLE 58. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS (USUALLY RICH IN STEARIC ACID)—continued.*

		Habitat	Component Fatty Acids Per Cent. (Wt.)				Method	Observers
			Palmitic	Stearic	Oleic	Linoleic		
Omphalocarpum boyankombo		Belgian Congo	←— 21 —→		79	—	L	Adriaens.[38]
Palaquium formosanum		Formosa	—	60(*u*)	40	—	L	Kafuku and Hata.[39]
„ *oblongifolium*	Njatuo tallow	Pacific Is.	6·5	57·5	36	—	L	de Jong and de Haas.[40]
„ „	Taban merah	Malaya	5·9(*v*)	54·0	39·9	—	F	Hilditch and Stainsby.[25]
Payena lancifolia	Surin kernel	Malaya, Borneo	—	ca. 58	ca. 42	—	L	Lewkowitsch.[41]
Sideroxylon cinereum	Morocco ironwood	U.S.A.	←— 14 —→		62	24	L	Dickhart.[56]
„ *ferrugineum*	Ironwood	Formosa	ca. 26(*w*)	—	57	17	L	Kafuku and Hata.[39]
„ „	„	Japan (?)	29·5	Trace	56·5	14	L	Nobori.[57]
CONVOLVULACEÆ								
Cuscuta reflexa		India	12·6	29·7	28·0	18·9(*x*)	F, H	Agarwal and Dutt.[42]
VERBENACEÆ								
Tectona grandis	Teak nut	India	6	19	←— 75 —→		L	Puntambekar and Krishna.[43]

(*a*) Also 0·7 per cent. myristic and 7·8 per cent. linolenic acids.
(*b*) Also 2·6 per cent. myristic and 0.8 per cent. arachidic acids.
(*c*) Also 2·4 per cent. arachidic acid.
(*d*) Also 1·3 per cent. arachidic acid.
(*e*) Also 0·7 per cent. arachidic acid.
(*f*) Also 3·3 per cent. erucic (?) acid.
(*g*) Also 0·3 per cent. myristic and 0·3 per cent. arachidic acids.
(*h*) Also 2·5 per cent. arachidic acid.
(*i*) Also 1·6 per cent. myristic and 1·8 per cent. arachidic acids.
(*j*) Also 2·3 per cent. myristic acid.
(*k*) Also 1·0 per cent. arachidic (?) acid.
(*l*) Also 1·4 per cent. myristic acid.
(*m*) Also 1·1 per cent. arachidic acid.
(*n*) Also 3·1 per cent. arachidic acid.
(*o*) Also 2·1 per cent. arachidic acid.
(*p*) Also 0·4 per cent. myristic acid.
(*q*) Also 16·3 per cent. myristic acid.
(*r*) Also 1·0 per cent. myristic and 3·3 per cent. arachidic acids.
(*s*) Also 1 per cent. arachidic acid.
(*t*) Also 1·1 per cent. arachidic and 0·7 per cent. hexadecenoic acids.
(*u*) Including small amounts of arachidic acid.
(*v*) Also 0·2 per cent. myristic acid.
(*w*) Including small amounts of myristic and stearic acids.
(*x*) Also 10·8 per cent. linolenic acid.
(*a′*) Also 1·8 per cent. arachidic acid.
(*b′*) Also 19·1 per cent. myristic acid.
(*c′*) Also 0·2 per cent. arachidic acid.
(*d′*) Also 1·2 per cent. myristic acid.
(*e′*) Also 6·3 per cent. arachidic acid.
(*f′*) Also 0·2 per cent. below C_{14}, 0·7 per cent. myristic, and 0·4 per cent. arachidic acids.
(*g′*) Also 1·6 per cent. lauric and 6·2 per cent. myristic acids.
(*h′*) Also 0·5 per cent. arachidic and 0·3 per cent. hexadecenoic acids.
(*i′*) Also 1·2 per cent. linolenic acid.
(*j′*) Also 0·7 per cent. linolenic acid.
(*k′*) Also 1·0 per cent. myristic and 3·1 per cent. arachidic acids.
(*l′*) Also 0·4 per cent. behenic acid.

* This was originally published[25] as the seed fat of *Sterculia fœtida*, but the fruits have subsequently been found not to be those of this plant, but of *Dacryodes rostrata*, a plant known with related *Canarium* sp. as "Java almond."

† Formerly classified as *Bassia*.

oleic acid prominent and linoleic acid a frequent component in variable proportions.

Sterculiaceæ seed fats : On the present evidence, this is one of the comparatively few botanical families in which seed fats of different genera and even species are markedly dissimilar in their component acids. The most familiar seed fat of the family, cacao butter (from *Theobroma cacao*), is a solid fat containing component acids palmitic 24, stearic 35, oleic 39, and linoleic 2 per cent., and thus falls in the same general group as the stearic-rich seed fats of many members of the Guttiferæ, Sapotaceæ and Dipterocarpaceæ.

On the other hand, the *Brachychiton* species has a seed fat low in palmitic and stearic acids, but with 73 per cent. oleic and 13 per cent. linoleic in its component acids, thus resembling a typical non-drying oil, whilst the genus *Sterculia* (which gives its name to the family) seems to have seed fats of varying types within its different species.

The seed fats of *S. tomentosa* (Sudan) and *S. platonifolia* (Japan) appear to be more or less similar in composition with about 25 per cent. saturated (palmitic and stearic) acids, 45 per cent. oleic acid, and the relatively high content of about 30 per cent. of linoleic acid. Those of " Java olive oil " (*S. fœtida*) and of *S. parviflora* are quite abnormal in that they contain large amounts of glycerides which on heating to 250° suddenly polymerise with considerable evolution of heat. The component acids of the seed fat of *S. fœtida* consist of about 15 per cent. of saturated (palmitic and myristic) acids, 13 per cent. of oleic acid, and over 70 per cent. of a very unusual unsaturated acid, $C_{19}H_{34}O_2$. The latter acid appears[113] to be a methyl-octadecadienoic acid, and is possibly 12-methyl-$\Delta^{9\ 11}$-octadecadienoic acid, $CH_3.[CH_2]_5.CMe:CH.CH.CH:CH.[CH_2]_7.COOH$. On oxidation it furnishes azelaic acid, *n*-heptanoic acid, and methyl *n*-hexyl ketone, which would support the structure suggested. The presence of a conjugated diethenoid system is also indicated by its behaviour with the Wijs iodine reagent, but the maleic anhydride (" diene ") value is lower than would be expected and neither the acid nor the oil itself show the ultra-violet absorption band which usually characterises conjugated diethenoid unsaturation in long-chain compounds. It is not known, however, whether the presence of the structure —CMe:CH.CH:CH— would alter the characteristic spectrum of the unsubstituted grouping —CH:CH.CH:CH—. Although, therefore, the constitution of the chief component acid of the seed fats of *S. fœtida* and *S. parviflora* must be considered uncertain, this acid is peculiar, and perhaps unique, among seed fatty unsaturated acids in possessing a branched chain and an uneven number of carbon atoms in its molecule.

The seed fats of the genus *Madhuca* in the Sapotaceæ require a further reference. In the first place, these have long been known to the technologist as " *Bassia* fats." The term *Bassia* was originally given to genera in two different orders, Chenopodiaceæ (1766) and Sapotaceæ (1771) ; the former having priority of date, Gmelin in 1791 assigned the term *Madhuca* to the Sapotaceæ genera concerned, and systematic botanists have since adopted this nomenclature, which is accordingly used here. Next, it will be seen that *Madhuca* seed fats are more variable than those of some other genera in this family in their composition, the stearic and palmitic acid contents in *M. latifolia, longifolia,* and *Mottleyana* being of somewhat the same order, with each ranging from about 15 to about 25 per cent. of the total acids.* Finally, the seed fat of *M. butyracea* is a complete exception to the rest of this genus and of the Sapotaceæ seed fats as a whole; its fatty acids include 56 per cent. of palmitic acid. and only 3 per cent. of stearic acid (the remainder being nearly all oleic acid). From the point of view of its major component acids, it belongs to the large group dealt with in Table 52, in which palmitic and oleic acids are major components and stearic acid a minor component. Indeed, the palmitic acid content of *M. butyracea* seed fat is the highest yet observed in any seed fat.

Apparently seed fats of the Burseraceæ family of plants may also form borderline cases between the palmitic-rich seed fats in Table 52 and the stearic-rich seed fats now being considered. At all events the few instances available (from the closely related genera *Canarium* and *Dacryodes*) include seed fats in which palmitic acid accounts for 30–40 per cent., and stearic for only 2–15 per cent., of the component acids, whilst in other cases the proportions of the two acids are reversed. For the present the Burseraceæ fats have been included in Table 58 with the others in which stearic, as well as palmitic, acid is a characteristic major component.

SEED FATS OF WHICH MYRISTIC AND LAURIC ACIDS ARE MAJOR COMPONENTS

Major component acids: LAURIC, MYRISTIC, palmitic, oleic.
Minor component acids: Caprylic, capric, stearic, linoleic.

We come, in conclusion, to a number of families in which seed fats are characterised by low contents of palmitic acid and also, more often than not, of oleic and linoleic acid, but in which the chief component is lauric or myristic acid (or sometimes both of these). The unsaturated acid content in a few cases exceeds 50 per cent. of the total acids, but is usually much less, in quite a number of instances only amounting to about 10 per cent. or even less of the mixed fatty acids.

The available quantitative data are collected in Tables 59A and 59B. The relatively large proportions of saturated acids of molecular weights 200 and 228, coupled with the presence of relatively small amounts of unsaturated acids, cause the mean saponification and iodine values of the fats to possess more significance than usual, and render it possible for the detailed figures in the table to be supplemented by others, based only on the saponification and iodine values, which are therefore given, under their respective families, in Table 59C.

A few notes are desirable with reference to each of the families included in Tables 59A, 59B, and 59C.

Ulmaceæ. The peculiarities of the elm seed fats, when contrasted with those of the seeds of most of the large trees of temperate climates, were remarked when dealing with the latter group (Tables 49 and 50, and p. 155). From the two analyses available it is evident that elm seed fats are characterised by the presence of very large proportions of glycerides of *n*-decanoic (capric) acid.

Lauraceæ. This family, from the typical genus of which *n*-dodecanoic acid was originally named, elaborates seed fats which in many cases seem to consist very largely of lauric, admixed with a smaller proportion of oleic, glycerides. Definite quantitative data are, as usual, not forthcoming in many cases but, when available, fully confirm this statement. The saponification and iodine values of the Lauraceous fats listed in Table 59C are consonant with the general belief that lauric acid is the major component of most of the seed fats of this family. The frequent substantial absence of other saturated acids renders the Lauraceæ seed fats extremely simple in composition, a feature which is also reproduced in some of the Myristicaceæ.

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* The analysis of *M. latifolia* seed fatty acids by Gill and Shah (Table 58, ref. 32) differs from all the other analyses in this group by including 16 per cent. of myristic acid with 27 per cent. of palmitic and only 2 per cent. of stearic acid.

Myristicaceæ. Here again the characteristic acid of the seed fats owes its common name to the nutmeg genus *Myristica*. The seed fats which have been studied come mainly from numerous species of the genus in question and the allied *Virola* ; they seem for the most part to be made up of relatively little oleic and palmitic acids with predominating amounts of myristic acid. As usual, fully quantitative analyses are few and recourse has to be made to more general statements, but there is no reason to doubt that myristic acid is the chief, often practically the only, saturated component of the seed fats of this family. The most recent work points to a minor difference in the component acids of seed fats of the genera *Myristica* and *Virola* : both seem to contain, as a rule, about 70 per cent. of myristic acid, but *Myristica* species have little or no lauric acid whilst *Virola* species may have 10–20 per cent. of lauric acid. Both types may have 10 per cent. or so of palmitic acid present in the seed fats.

Simarubaceæ. It seems that, as in Euphorbiaceæ and one or two other families, this is a case in which seed fat composition is specific to various genera rather than to the order as a whole. The *Irvingia* seed fats for which we have data seem to consist of minor amounts of oleic with a mixture of myristic and lauric acids as the major component (and thus fall in the group listed in Table 59A). Those of the genus *Picramnia*, as we have seen earlier (p. 181), contain a mixture of acids in which the unusual acetylenic tariric acid appears, and those of *Picrasma* include petroselinic acid (p. 179) as a major component ; whilst the analyses of *Perriera* and *Ailanthus* fats place these in the same large category of palmitic-oleic-linoleic seed fats which was dealt with in Table 52 (pp. 172–175).

Vochysiaceæ. The analyses of a seed fat from this family (Jaboty kernel fat) also place it in a class in which lauric, myristic, and palmitic are the main saturated acids present in quantity.

Salvadoraceæ. The earlier data of Patel *et al.* seemed to show that these berried shrubs of India and N.W. Asia contained fats remarkably similar to those of the Palmæ, from which, of course, they are far removed botanically. The later study of Gunde, carried out on material specially collected in the Punjab by the Indian Forestry Service, indicates, however, that both species examined contained almost identical fats, the component acids of which consisted of about 50 per cent. of myristic acid with about 20 per cent. each of lauric and palmitic acids, and about 5 per cent. of oleic acid.

Palmæ. The seed fats of the palms are perhaps more striking than those of any other natural order of plants, because on the one hand they contain an extremely unusual and varied mixture of saturated acids, and on the other hand this mixture persists with remarkably little quantitative variation throughout the whole family, with very few exceptions. (In the Batava and date palms, the endosperms contain only small quantities of fat, and the saponification and iodine values of the latter indicate more unsaturated acids and acids of higher molecular weight than in any other instances :

TABLE 59A. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS (USUALLY RICH IN LAURIC AND/OR MYRISTIC ACIDS)*

[For Palmæ seed fats, see Table 59B.]

Major component acids: LAURIC, MYRISTIC, palmitic, oleic.
Minor component acids: Caprylic, capric, stearic, linoleic.

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.)					METHOD	OBSERVERS
			SATURATED			OLEIC	LINOLEIC		
			LAURIC	MYRISTIC	PALMITIC				
ULMACEÆ									
Ulmus americana	American elmseed	U.S.A.	5·9(*a*)	4·6	2·9	11·0	9·0	F	Schuette *et al.*[1]
„ *campestris*	Elmseed	Europe	[Total acids, mean equivalent ca. 190, iod. val. 18·4, R-M val. 3·8, 50 per cent. capric acid.]						Pawlenko; Beythien *et al.*[2]
MYRISTICACEÆ									
Myristica fragrans syn.	Nutmeg	East Indies	1·5	76·6	10·1	10·5	1·3	F	Collin and Hilditch.[3]
officinalis	„	„ „	—	60	32	8	—		Heiduschka and Häbel.[4]
„ *malabarica*		South India	—	39·2	13·3(*b*)	44·1	1·0	F	Collin and Hilditch.[3]
Pycnanthus Kombo	Kombo nut	Sierra Leone	10·2	56·8	3·6	5·7(*c*)	—	F	Atherton and Meara.[5]
Virola (myristica) Bicuhyba	Ucuhuba nut	S. America	13·3	66·6	8·9 (*d*)	6·6	3·0	F	Steger and van Loon.[6]
„ „ „	„ „	„	5	73	11	11	—	F	Ramos and de Nascimento.[7]
„ „ *otobo*	Otobo nut	„	20·8	73·4	0·3	5·5	—	F	Baughman *et al.*[8]
„ „ species	Virola nut	„	14·9(*e*)	73·2	5·0	6·4	—	F	Atherton and Meara.[5]
„ „ „	„ „	„	13·3	66·6	8·9(*q*)	6·6	3·0	F	Verkade and Coops.[9]
LAURACEÆ									
Actinodaphne Augustifolia		India	ca. 90	—	—	ca. 10	—		Puntambekar.[10]
„ *Hookeri*		„	96	—	—	4	—		Puntambekar and Krishna.[10]
Cinnamomum camphora	Cinnamon	India	95	—	—	5	—		Puntambekar.[10]
Laurus nobilis	Laurel, bay kernel	S. Europe,	35·0	—	9·7	36·6	18·7	F	Collin and Hilditch.[3]
„ „	„ „ „	India, etc.	43·1	—	6·2	32·3	18·4	F	Collin.[11]
Lepidadenia Wightiana	Tangkallak kernel	East Indies	87 (?)	—	—	13 (?)	—		Sack.[12]
Litsea chinensis		India	93	—	—	7	—		Puntambekar.[10]
„ *citrata*		„	ca. 95	—	—	ca. 5	—		„
„ *longifolia*		Ceylon	88·3	—	3·4(*r*)	5·9	Trace	F	Child and Nathanael.[78]
„ *zeylanica*		India	70	—	—	30 (?)	—		Puntambekar.[10]
Neolitsea involucrata	Dawul-Kurundu seed	Ceylon	85·9(*f*)	3·8	—	4·0	3·3	F	Gunde and Hilditch.[13]

SIMARUBACEÆ									
Ailanthus glandulosa		Transcaucasia	—	—	9·8(*g*)	82·0	5·5		Michelson.[14]
Irvingia Barteri	Dika nut	Nigeria	38·8	50·6	—	10·6	—	F	Collin and Hilditch.[15]
,, *gabonensis*	,, ,,	,,	19·5	70·5	—	10	—	F	Pieraerts.[16]
,, ,,	,, ,,	,,	58·6(*h*)	33·4	2·0	1·8	—	F	Bushell and Hilditch.[17]
,, *Oliveri*	Cay-Cay nut	Indo-China	ca. 39	ca. 56	—	ca. 5	—	F	Bontoux.[18]
Perriera Madagascariensis	Kirondro seed	Madagascar	—	—	17·5	62·5	20	L, H	Volmar and Samdahl.[19]
Picramnia Lindeniana	Tariri	Central America	—	ca. 22	ca. 33	ca. 22(*i*)	—		Grimme.[20]
,, *Sow*	,,	,, ,,	←—— 5 ——→			(*j*)	—		Steger and van Loon.[21]
Picrasma quassioides	Nigaki seed	Japan, China	←—— 23·3(*k*) ——→			←— (*k*) —→			Tsujimoto and Koyanagi.[22]
VOCHYSIACEÆ									
Erisma calcaratum	Jaboty kernel	Brazil	—	28·0	43·6(*l*)	25·0	—		Margaillan.[23]
,, ,,	,, ,,	,,	23·9	52·8	18·9	2·8	—(*m*)	F	Steger and van Loon.[24]
SALVADORACEÆ									
Salvadora oleoides	Khakan kernel	India, Persia	47·2(*n*)	28·4	—	12·0	1·3	F	Patel *et al.*[25]
,, ,,	,, ,,	India	21·2(*o*)	52·9	18·9	5·5	—	F	Gunde and Hilditch.[26]
,, *persica*		,,	19·6(*p*)	54·5	19·5	5·4	—	F	,, ,,

(*a*) Also 5·3 per cent. octanoic and 61·3 per cent. decanoic (capric) acids.
(*b*) Also 2·4 per cent. stearic acid.
(*c*) Also 23·7 per cent. tetradecenoic acid.
(*d*) Also 1·6 per cent. stearic acid.
(*e*) Also 0·5 per cent. capric acid.
(*f*) Also 3·0 per cent. capric acid.
(*g*) Also 2·4 per cent. stearic and traces of linolenic acids.
(*h*) Also 3·1 per cent. capric and 1·1 per cent. stearic acids.
(*i*) Also ca. 20 per cent. *tariric* (Δ^{6}-octadecynoic) acid and ca. 3 per cent. stearic acid.
(*j*) Almost wholly (95 per cent.) tariric (Δ^{6}-octadecynoic) acid.
(*k*) Saturated acids chiefly palmitic, with perhaps myristic and lauric; unsaturated acids largely consist of petroselinic (Δ^{6}-octadecenoic) acid.
(*l*) Also 3·4 per cent. stearic acid.
(*m*) Also 1·6 per cent. " residual acids."
(*n*) Also 4·4 per cent. caprylic and 6·7 per cent. capric acids.
(*o*) Also 1·5 per cent. capric acid.
(*p*) Also 1·0 per cent. capric acid.
(*q*) Also 1·6 per cent. stearic acid.
(*r*) Also 2·4 per cent. stearic acid.

TABLE 59B. *COMPONENT ACIDS (WTS. PER CENT.) OF SEED FATS OF THE PALMÆ*

Major component acids : LAURIC, MYRISTIC, palmitic, oleic.
Minor component acids : Caprylic, capric, stearic, linoleic.

		HABITAT	COMPONENT FATTY ACIDS PER CENT. (WT.)								METHOD	OBSERVERS
			SATURATED						OLEIC	LINOLEIC		
			C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}				
Acrocomia sclerocarpa	Grugru kernel	Brazil, W. Indies	*7·8	5·6	44·9	13·4	7·6	2·6	16·5	1·6	F	Collin.[27]
Areca catechu	Areca, betel nut	Pacific Is.	—	1·0	43·6	21·0	3·1	2·3	29·0	—		Rathje.[28]
,, ,,	,, ,, ,,	,, ,,	—	1·0	53·7	24·9	2·5	3·3	14·6	—		,,
Astrocaryum Murumuru	Murumuru kernel	Brazil	1·1	1·6	42·5	36·9	4·6	2·1	10·8	0·4	F	Saraiva.[29]
,, *Tucuma*	Tucuma ,,	Brazil, W. Indies	1·3	4·4	48·9	21·6	6·4	1·7	13·2	2·5	F	Collin.[27]
Attalea cohune	Cohune nut	Honduras	*7·5	6·6	46·4	16·1	9·3	3·3	9·9	0·9	F	Hilditch and Vidyarthi.[30]
,, *excelsa* (syn. *Syagrus coronata*)	Ouricoury nut	Central America, Brazil	*9·8	8·2	45·8	9·0	7·7	2·3	13·1	2·2	F	McKinney and Jamieson.[31]
,, *funifera* (syn. *Orbignia speciosa*)	Babassu kernel	Brazil, Mexico, W. Africa	*6·5	2·7	45·8	19·9	6·9	—	18·1	—	F	Heiduschka and Agsten.[32]
,,	,, ,,	Brazil	4·1	7·6	45·1	16·5	5·8	5·5	11·9	2·8	F	Nobori and Ono.[79]
,, ,,	,, ,,	,,	*4·8	6·6	44·1	15·4	8·5	2·7(*e*)	16·1	1·4	F	Jackson and Longenecker.[83]
Cocos nucifera	Coconut	Tropical coasts	9·5	4·5	51·0	18·5	7·5	3·0	5·0	1·0	F	Armstrong *et al.*[33]
,, ,,	,,	,, ,,	*8·7	5·6	45·0	18·0	(←—not estimated—→)				F	Taylor and Clarke.[34]
,, ,,	,,	,, ,,	*7·9	7·2	48·0	17·5	9·0	2·1	5·7	2·6	F	Collin and Hilditch.[35]
,, ,,	,,	,, ,,	*7·8	7·6	44·8	18·1	9·5	2·4	8·2	1·5	F	Child and Collin.[36]
,, ,,	,,	,, ,,	*9·0	6·8	46·4	18·0	9·0	1·0	7·6	1·6	F	Lepkovsky *et al.*[37]
,, ,,	,,	,, ,,	5·4(*a*)	8·4	45·4	18·0	10·5	2·3	7·5	Trace	F	Longenecker.[80]
,, ,,	,,	S. China	8·7	8·1	51·3	13·1	7·5	2·0(*b*)	5·5	2·3	F	Nobori.[81]
,, ,,	,,	South Sea Is.	9·2(*c*)	9·7	44·1	15·9	9·6	3·2	6·3	1·5	F	Nobori and Kawabata.[81]
,, *pulposa*	,,	Uruguay	10·4(*d*)	14·4	37·1	7·1	1·8	1·3	23·7	2·6	F	Jamieson and Rose.[82]
Elæis guineensis	Palm kernel	W. Africa	3·0	3·0	52·0	15·0	7·5	2·5	16·0	1·0	F	Armstrong *et al.*[38]
,, ,,	,, ,,	(E. Indies)	2·7	7·0	46·9	14·1	8·8	1·3	18·5	0·7	F	Collin and Hilditch.[35]
,, ,,	,, ,,	,,	4·3	4·8	51·3	16·5	7·6	1·7(*f*)	11·3	1·3	F, S	Carsten *et al.*[84]
,, ,,	,, ,,	,,	3·9	6·3	51·2	17·5	6·5	2·0(*g*)	10·5	1·2	F, S	,, ,, [84]
Hyphæne thebaica	Doum palm nut	Tropical Africa	1·3	2·8	31·8	14·8	13·8	4·8	←—30·7—→		F	Ubaldini.[39]
Manicaria saccifera	Turluru kernel	Brazil, W. Indies	*5·3	6·6	47·5	18·9	8·2	2·4	9·7	1·4	F	Collin.[27]
Palma campestris	Butia palm fruit	Tropics	←——30——→			←—— 25 ——→			32	13	B, T	Kaufmann and Baltes.[40]
Roystonia oreodoxa	Cuban palmiche nut	Central America	—	5·0	32·2	16·1	7·5	1·0	28·7	9·5	F	Stillman and Reed.[41]

* Traces of *n*-hexanoic (caproic) acid ; 0·5 per cent. in coconut oil (Taylor and Clarke,[34] Lepkovsky *et al.*[37]).

(*a*) Also 0·8 per cent. hexanoic, 0·4 per cent. arachidic, and 1·3 per cent. hexadecenoic acids.

(*b*) Also 1·5 per cent. arachidic acid.

(*c*) Also 0·3 per cent. hexanoic and 0·2 per cent. arachidic acids.

(*d*) Also 1·6 per cent. hexanoic acid.

(*e*) Also 0·2 per cent. arachidic acid.

(*f*) Also 0·6 per cent. arachidic and 0·6 per cent. hexadecenoic acids.

(*g*) Also 0·5 per cent. arachidic and 0·4 per cent. hexadecenoic acids.

TABLE 59C

The following kernel fats have saponification values and iodine values which indicate probable close resemblance in component fatty acids to those in Tables 59A and 59B.

		HABITAT	SAP. VALUE	IODINE VALUE
PALMÆ				
Acrocomia Total	Paraguay palm kernel	S. America	240–247	24–28[42]
,, *(Mauritia) vinifera*	Coyol, muriti palm kernel	Central America	246	25[43]
Astrocaryum aculeatum, vulgare.	Aouara, tucum kernel	S. America	240–249	10–14[44]
,, *Jauari*	Awarra kernel	Brazil	242	13–15[45]
,, *Paramaca*	Paramaca kernel	Guiana	257	14[46]
,, *segregatum*		,,	238	17[46]
Attalea spectabilis	Curua palm kernel	W. Africa	259·5	8·9[47]
Bactris acanthocarpa		Guiana	238	15[48]
,, *Plumeriana*		,,	(chiefly lauric acid)[49]	
Butea bonneti	Bonneti palm kernel (Caucasus)	Caucasus	260	24[50]
Cocos Syagrus	Piririma kernel	Brazil	252	12–13[44]
Copernicia cerifera	Carnauba kernel	,,	221	23[51]
Elæis melanococca	Cayau, Noli palm kernel	Central and S. America	234	27–28[52]
Hyphæne Schatan		Madagascar	245	22[53]
Jubæa chinensis	Honey palm kernel	Chile	273	13[54]
Maximiliana regia	Cokerite kernel	Brazil, Guiana	240–253	7–16[55]
Roystonia regia	Cuban royal palm kernel	Central America	237	32[48]
Scheelea insignis, regia	Corozo (Mamarron) palm kernel	Central America	251	10[56]
Œnocarpus distichus	Batava palm kernel	Brazil	contains only 1–7 per cent. of oil, S.V. 209, I.V. 55.[57]	
Phœnix dactylifera	Date kernel	N. Africa, Canary Islands	contains only 8 per cent. of oil, S.V. 211, I.V. 52.[58]	
MYRISTICACEÆ				
Cælocaryum cuneatum		Cameroons	(similar to nutmeg butter.)	33[59]
Myristica argentea		New Guinea	,,	[60]
,, *canarica*	Mangalore butter	Tropics	215	26[61]
,, *ocuba*		Brazil	(similar to nutmeg butter.)	[62]
,, *platysperma*		Brazil	240	5–6[63]
Staudtia Kamerunensis		Cameroons	chiefly myristic and oleic acids)[64]	
Virola guatemalensis		Central America	244	14[65]
,, *Micheli*		,, ,,	(chiefly myristic and oleic acids)[66]	
,, *sebifera*		W. Indies	,,	,, [67]
,, *surinamensis*		,,	,,	,, [68]
,, *venezuelensis*		Central America	221	12 [65]
LAURACEÆ				
Acrodiclidium mahuba		Brazil	272	20 (chiefly lauric)[69]
Cinnamomum camphora	Camphor seed	Japan	284	4·5 (chiefly lauric)[70]

TABLE 59C—*continued*

		HABITAT	SAP. VALUE	IODINE VALUE
LAURACEÆ—*continued*				
Lindera benzoin	Fever bush seed	N. America	284	? (chiefly lauric)[71]
„ *hypoglauca*		Japan	223	69[72]
„ *præcox*		„	274	20[73]
„ *sericea*		„	256	65[73]
„ *triloba*		„	282	12[73]
Litsea polyantha		India	245	34 (chiefly lauric)[74]
„ *Stocksii*		„		(„)[75]
„ *zeylanica*		„	245	46 (chiefly lauric)[75]
Machilus Thunbergii		Japan	241	66[70]
Nectandra Wane		Guiana	270	3[76]

NOTE.—*Lindera* and *Tetradenia* seed fats (Japan) contain small amounts of mono-ethylenic C_{12} and C_{14} acids.

SALVADORACEÆ				
Salvadora persica	Mustard tree	India, N. Africa	245	6[77]

this may, of course, be due to the presence of more testa fat than usual with the endosperm fat.)

Lauric acid forms 45–50 per cent. of the total fatty acids of most of the endosperm fats, whilst myristic acid amounts as a rule to about 20 per cent.; characteristic also is the presence, in smaller quantities, of capric and caprylic acids, $C_{10}H_{20}O_2$ and $C_8H_{16}O_2$, but the proportions of palmitic and stearic acids are respectively only about 7–9 and 2–3 per cent. The studies of Taylor and Clarke, Longenecker, Nobori, and some others (for literature references see Table 59B) show that coconut oil fatty acids also contain very small proportions (0·3–0·8 per cent. wt.) of *n*-hexanoic (caproic) acid, and probably also the customary traces of hexadecenoic acid. Witgert [114] carried out an intensive fractional distillation of the methyl esters of 25 kilograms of coconut oil fatty acids, and found that over 99·5 per cent. of the acids belonged to the even-numbered series of acids from C_8 upwards; he isolated, however, small amounts of nonanoic (0·3 g.), undecanoic (0·2 g.) and tridecanoic (0·4 g.) acids and considered that the existence of traces of these acids in coconut oil is established, but that their combined amount does not exceed 0·1 per cent. of that of the even-numbered acids. Witgert suggests that the presence in these minute proportions of odd-numbered acids (which may well be due to secondary decomposition changes) does not invalidate the statement that, substantially, only fatty acids containing an even number of carbon atoms in the molecule are synthesised in the plant.

The extent to which the characteristic acids of the Palmæ are quantitatively reproduced in the data for eleven out of fifteen species (of the genera) in Table 59B, supplemented by the average analytical characteristics added in Table 59C for many other species (practically all of which are close to those of, for example, coconut or palm kernel oils, sap. values 250–260 and 243–250, and iodine values 8–10 and 15–20 respectively), is extraordinary.

The figures referred to are, of course, those for the fats present in the endosperm of the seed. The thin testa of the seeds also contains fatty matter, and the composition of the testa fat is not the same as that of the endosperm. This was first noticed by Richardson [78] in the case of the testa fat of the coconut, whilst Allan and Moore[77a] subsequently found that the testa fats of a number of other Palmæ seeds were similar in character. The fat content of the testa is less than that of the endosperm, and the testa fat contains more of the unsaturated, and less of the saturated acids, than that of the endosperm. Thus, Armstrong, Allan, and Moore,[77b] and Carsten, Hilditch, and Meara,[78] record respectively the following component acids for testa and endosperm fats from the coconut (*Cocos nucifera*) and the West African oil palm (*Elæis guineensis*):

COMPONENT ACIDS	COCONUT		PALM KERNEL	
PER CENT.	TESTA	ENDOSPERM	TESTA	ENDOSPERM
Caprylic	2 (?)	9·5	0·6	4·3
Capric	2	4·5	4·4	4·8
Lauric	28	51·0	35·7	51·3
Myristic	22	18·5	16·0	16·5
Palmitic	12	7·5	10·7	7·6
Stearic	1 (?)	3·0 (?)	1·5	1·7
Oleic	23	5·0	26·0	11·3
Linoleic	10	1·0	5·0	1·3

The fat content and the saponification and iodine values of the fats from the testa and endosperm of various seeds of the Palmæ, as given by Allan and Moore (*loc. cit.*), are shown in Table 60.

TABLE 60

SPECIES	COMMON NAME	TESTA FAT			ENDOSPERM FAT		
		PER CENT. FAT IN TESTA	SAP. VAL.	IOD. VAL.	PER CENT. FAT IN ENDOSPERM	SAP. VAL.	IOD. VAL.
Attalea funifera	Babassu	49	232·5	22·8	66	257·5	10·2
Attalea maripa	Ouricoury	56	241	30·4	70	261·7	10·5
Cocos nucifera	Coconut	22–58	221–241	21·5–59·7	55–75	255·5–262·5	5·7–9·3
Elæis guineensis	Oil palm	30–33	229·5–233·3	28·0–29·6	56	244	12·4

Thus testa fat, in seeds of the Palmæ, has a composition intermediate between those of the fruit-coat fat and the endosperm fat, but is distinctly more akin to the latter.

Component Acids of Seed Phosphatides

Seeds contain phosphatides as well as glycerides, but the amounts of phosphatides are usually very small, and are frequently only about 0·1–0·2 per cent. of that of the glycerides which are also present.* Doubtless owing to this circumstance, the fatty acids present in combination in phosphatides from the vegetable kingdom have received less notice hitherto than those from animal sources. Until Levene and Rolf[80] published the results of their study of soya bean phosphatides, plant phosphatides were usually supposed to be varieties of lecithin and the only acid components which had been reported were palmitic, stearic, and oleic—in the " lecithins " respectively of leguminous seeds,[81] sugar cane,[82] and beet root.[83] Levene and Rolf,[80] in the case of soya bean phosphatides, showed that more than one type was present, including products less soluble in alcohol than lecithin, and that the phosphatides sparingly soluble in alcohol and also the alcohol-soluble forms gave optically active barium glycerophosphate, indicating that the phosphoric acid was combined with an α-glyceryl hydroxyl group. They identified palmitic, stearic and (in the form of bromo-additive products) oleic, linoleic, and linolenic acids in the mixed fatty acids; they concluded that in the alcohol-soluble phosphatides (choline compounds) the proportion of saturated acids was lower than in animal lecithin, whereas the alcohol-insoluble compounds (β-aminoethanol derivatives) showed no marked difference in this respect from animal kephalin.

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* Goldovski and Lischkevitsch[79] state that expressed sunflower seed, cottonseed, and groundnut oils contain 0·03–0·06 per cent. of phosphatides, but that the same oils, obtained by extraction with light petroleum, contained somewhat more—0·2–0·4 per cent.

Recently Jamieson *et al.*[84] have further discussed the separation of the mixture of phosphatidic compounds present in soya beans, and have put forward evidence that in the seed the phosphatides may be united with carbohydrates in compounds resembling glucosides. On the other hand, Rewald[85a] holds that, although plant phosphatides are closely associated with carbohydrates in the seed, the union is not of a chemical nature, since by appropriate physical methods (e.g. extraction from an aqueous emulsion with a suitable solvent) the phosphatides can be separated in a relatively pure condition and free from either carbohydrate or fat.

Woolley and White[115] have separated from crude soya bean phosphatides small quantities of a compound, lipositol, which appears to be very similar to the phospholipids of the brain and spinal cord. It is composed of inositol, galactose and *d*-tartaric acid (in equimolecular proportions), united with phosphoric acid, ethanolamine and a fatty acid mixture which includes saturated (about 5 per cent. cerebronic, 65 per cent. palmitic and 30 per cent. stearic acid) and unsaturated (oleic and probably other) acids.

Suzuki *et al.*[86] also studied the phosphatides of soya beans, and confirmed the presence of alcohol-insoluble " kephalin " and alcohol-soluble " lecithin " derived respectively from β-aminoethanol and choline. They also brominated the phosphatide fractions and isolated various crystalline derivatives containing mixtures of fatty acids, from which the presence of " mixed " compounds such as palmito-oleo-, or oleolinoleo-, as well as dioleo- and dilinoleo-phosphatides was established. Suzuki and Yokoyama[86] separated, by means of cadmium chloride double salts, α- and β-" lecithins " from soya beans, and studied the mixed fatty acids from each group by bromination.

Diemair, Bleyer, and Schmidt[87a] examined the fatty acids from the phosphatides present in barley, wheat, and oats to the respective extents of 0·16, 0·12, and 0·14 per cent. They separated the acids by the lead salt method into " solid " and " liquid " portions; the " solid " acids were mainly palmitic acid, whilst the crystalline tetrabromo-adduct (m.p. 114°) of seed fat linoleic acid was readily isolated from all the " liquid " acids. Their quantitative data included the following:

PHOSPHATIDES OF:	BARLEY	WHEAT		OATS
P:N ratio	1:1·01	1:1·06	1:1·03	1:1·02
Yield of fatty acids (per cent.)	69·1	59·0	62·4	62·5
" Solid " acids (per cent.)	14·8	16·7	16·5	12·2
" Liquid " acids (per cent.)	84·6	83·3	73·4	86·1
Iodine value of " liquid " acids	ca. 170	135·0	141·2	198·3

If these data are compared with those for the corresponding Gramineæ seed fats in Table 53 of this chapter, it will be seen that the proportion of saturated acids is somewhat higher in the phosphatide than in the glyceride fatty acids, and that the phosphatide unsaturated fatty acids contain much more linoleic (and possibly linolenic) acids than the corresponding portions of the glyceride acids.

The phosphatides of the leaves of grasses, as distinct from the seed phosphatides, have been shown to resemble those of leaves of other plants in that they contain calcium and potassium salts of phosphatidic acids in addition to the true phosphatides (choline or β-aminoethylalcohol salts of these acids) (*cf.* Chibnall *et al.*[17, 18, 19]). Smith and Chibnall[19] stated that the phosphatides in cocksfoot grass are thus constituted, and that the fatty acids present include higher proportions of unsaturated than of saturated acids. Shorland[97] found 2·4 per cent. of total phosphatides in the lipids of mixed New Zealand pasture grasses, and also found that the phosphatide fatty acids of cocksfoot grass (*Dactylis glomerata*) resembled those of the corresponding glycerides in composition, except that the unsaturated C_{18} acids had a somewhat lower mean unsaturation (—3·7 to —4·8H) than in the case of the glycerides (—5·0 to —5·3H).

An analysis of dried grass by Rewald[85b] indicated the presence of about 7·3 per cent. of total lipids, much of which was fat; phosphatides amounted to 0·5–1 per cent. of the dried grass, but other organic compounds containing phosphorus were also present.

Rewald[85c] gives the following proportions of lecithin (alcohol-soluble phosphatides) and kephalin (alcohol-insoluble) in the phosphatides of various seed endosperms.

	Groundnut Per Cent.	Cottonseed Per Cent.	Linseed Per Cent.	Sunflower Per Cent.	Sesame Per Cent.
Lecithin	35·7	28·8	36·2	38·5	52·2
Kephalin	64·3	71·2	63·8	61·5	40·6

Sesame seed phosphatides also contain 7·2 per cent. of a fraction soluble in hot but insoluble in cold alcohol.

Roth and Schuster,[116] however, state that most seed phosphatides contain 70–80 per cent. of lecithin with 30–20 per cent. of kephalin.

Tristram[117] obtained about 0·1 per cent. of phosphatides from the rubber latex of *Hevea brasiliensis*, and found that these consisted of about equal proportions of lecithin and of the calcium and potassium salts of phosphatidic acids (*cf.* p. 137). The phosphatide fatty acids had iodine values of 90–112 and contained 21–26 per cent. of saturated acids and 79–74 per cent. of unsaturated acids (including oleic and linoleic).

Diemair and Weiss[87b] observed that the proportions of lecithin and kephalin in the seed phosphatides of lupins are respectively about 74 and 26 per cent. The lupin lecithin fatty acids consisted of about 16 per cent. saturated (palmitic and traces of arachidic) and 84 per cent. unsaturated (oleic, linoleic and linolenic). α- and β-Glycerophosphoric acids were both present, the former in greater amount. Bleyer, Diemair, and Weiss[87c] found that rape seed lecithin contained about 77 per cent. of α-, and 23 per cent. of β-glycerophosphoric acid, and that its fatty acids included about 16 per cent. saturated and 84 per cent. unsaturated components. Heiduschka and Neumann[88] report 18 per cent. of palmitic, 25–28 per cent. of oleic and

45 per cent. of linoleic acid in rape seed phosphatides, but do not mention erucic or hexadecenoic acids (*cf.* below).

That linoleic acid is the most characteristic, and usually the most prominent, component of seed phosphatide fatty acids is also shown by detailed (ester-fractionation) analyses carried out by Hilditch, Pedelty, and Zaky [89] on the acids of soya bean, rape seed, cottonseed, sunflower seed, groundnut and linseed phosphatides. Table 61 shows the weight percentages of the component acids in alcohol-insoluble and alcohol-soluble fractions of soya bean and rape seed phosphatides, and of the combined phosphatides from the other four seeds, together with those of the corresponding glycerides (*cf.* Tables 57, ref. 26; 56, ref. 4; 52, ref. 68; 50, ref. 62; 57, ref. 9; 49, ref. 35, respectively).

TABLE 61. *COMPONENT ACIDS OF SOYA BEAN AND RAPE SEED GLYCERIDES AND PHOSPHATIDES (WTS. PER CENT.)*

	SOYA BEAN			RAPE SEED	
	GLYCERIDES	PHOSPHATIDES		GLYCERIDES	PHOSPHATIDES
		ALCOHOL-INSOLUBLE	ALCOHOL-SOLUBLE		ALCOHOL-INSOLUBLE
Myristic	Trace	—	—	—	1
Palmitic	10	12	19	2	8
Stearic	2	4	—	—	—
Arachidic	1	1	—	—	—
as Behenic	—	—	—	1	2
Hexadecenoic	0·5	9	6	Trace	2
Oleic	25·5	10	18	17	22
Linoleic	58	55	52	29	42
Linolenic	3	4	4	—	—
as C_{20} unsaturated	—	5	1	—	—
Erucic	—	—	—	51	23

	COTTONSEED		SUNFLOWER		GROUNDNUT		LINSEED	
	GLYC.	PHOS.	GLYC.	PHOS.	GLYC.	PHOS.	GLYC.	PHOS.
Myristic	1·5	—	—	—	—	—	Trace	—
Palmitic	23	17	6	15	8	16	5	11
Stearic	1	7	2	5	3	3	3·5	11
Arachidic	1·5	3	1	10	—	—	0·5	—
as C_{20}, C_{22}, C_{24}	—	—	—	—	7	7	—	—
Hexadecenoic	2	2	—	—	—	—	—	4
Oleic	23	20	25	19	56	47	19	34
Linoleic	48	45	66	46	26	23	24	20
Linolenic	—	—	—	—	—	—	47	17
as Unsaturated C_{20-22}	—	6	—	5	—	4	—	3

A later ester-fractionation and thiocyanometric (T) analysis of the fatty acids of purified soya bean phosphatides (97 per cent. lecithin and 3 per cent. kephalin) by Thornton *et. al.*[118] showed palmitic 16, stearic 6, oleic 13, linoleic 63, and linolenic 2 per cent. (wt.).

From the six instances in Table 61 (which cover a fairly wide range of botanical families) the following generalisations may be suggested tentatively:

(i) Seed phosphatides contain characteristic, although minor, proportions of highly unsaturated C_{20} and C_{22} acids which are not present in the corresponding glycerides.

(ii) Acids of the saturated series form a greater proportion of seed phosphatide than of seed glyceride fatty acids; palmitic acid seems usually to amount to at least 12–15 per cent. of the phosphatide fatty acids.

(iii) All the acids present in any seed glyceride are also found in the corresponding seed phosphatide.

(iv) Linoleic acid is on the whole the most characteristic acid of seed phosphatides. Although, in two instances out of the six in Table 61 it amounts to only 20–25 per cent. of the total acids, in the others it forms 45–55 per cent. of the total phosphatide acids. The relative amounts of oleic and linoleic acid are also interesting. In soya beans and rape seed the ratio of linoleic to oleic acid is greater in the phosphatides than in the glycerides ; in cottonseed and sunflower seed it is much the same in both lipids ; whilst in groundnut and linseed it is definitely lower in the phosphatides than in the glycerides. In linseed, indeed, the relative proportions of oleic, linoleic and linolenic acids in the glycerides are reversed in the phosphatides.

(v) Hexadecenoic acid, which is found as a minor component in all animal phosphatides, is also present in small quantities in some seed phosphatides, but in others (e.g. sunflower seeds and groundnuts) it appears to be absent.

In proportions of saturated acids, and in the presence of highly unsaturated C_{20-22} acids, there is marked resemblance between the phosphatides of vegetable and animal fats, especially when these are compared with the corresponding glycerides. The vegetable phosphatides are perhaps distinguished in that they contain all the fatty acids which occur in the corresponding seed glycerides, and by the general prominence of linoleic acid amongst the component fatty acids. Moreover, the linoleic acid of the plant phosphatides is the form present in seed glycerides, furnishing nearly 50 per cent. of the crystalline tetrabromo-additive product of m.p. 114°. Possibly linoleic acid has a specific function in the phosphatides of seeds, but in the absence of a much wider range of information this suggestion is only speculative.

It will, in general, be clear from the foregoing section that comparisons which have been made from time to time on the basis only of the iodine values of mixed fatty acids of phosphatides or glycerides are of little value without some form of detailed analysis—at the least, a determination of the proportions of saturated acids.

General Conclusions

It may be well to conclude this somewhat unwieldy chapter by summarising the main conclusions which have been reached :

(i) The almost exclusive fatty components of the leaf, stem, root, and fruit-coat of all plants are palmitic, oleic, linoleic (and sometimes linolenic) acids ; unsaturation is most evident in the C_{18} acids of the leaf, and least so in the storage fats of fruit-coat and roots.

(ii) These acids are also the main components of many seed fats ; but, equally, one or more of a number of other acids, saturated and unsaturated, is frequently found in quantity in numerous seed fats.

(iii) The fatty (glyceride) components of seeds are specific and closely related to the families in which the parent plants have been grouped by botanists. It is, indeed, not an exaggeration to say that the component acids of seed fats could themselves be made the basis of a system of classification of plants.

(iv) Seed phosphatides have been relatively little studied. The few results available suggest that linoleic acid is often the most prominent fatty acid in these compounds ; but the characteristic acids of the corresponding seed glycerides are also found, usually in relatively smaller proportions than in the latter. Seed phosphatides may resemble animal phosphatides in possessing an increased proportion of saturated acids as compared with the corresponding glycerides, the increase being in palmitic acid in the vegetable, as contrasted with increase in stearic acid in the animal kingdom ; also, seed phosphatides may contain appreciable amounts of unsaturated C_{20} acids, these being absent from the glycerides.

(v) Perusal of the tables included in this chapter will indicate the scope for further detailed information regarding the component acids of fats from all parts of plants. It is not beyond our province, it may be hoped, to point out that work of this nature is only useful when it is as quantitative as possible, when quantitative data are substantiated by careful evidence as to the individuality of at least the chief component acids, and, above all, when the identity of the species from which the fat is derived is known with certainty.

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(iv) Seed phosphatides have been relatively little studied. The few results available suggest that linoleic acid is often the most prominent fatty acid in these compounds; but the characteristic acids of the corresponding seed glycerides are also found, usually in relatively smaller proportions than in the latter. Seed phosphatides may resemble animal phosphatides in possessing an increased proportion of saturated acids as compared with the corresponding glycerides, the increase being in palmitic acid in the vegetable, as contrasted with increase in stearic acid in the animal kingdom; also, seed phosphatides may contain appreciable amounts of unsaturated C_{20} acids, these being absent from the glycerides.

(v) Perusal of the tables included in this chapter will indicate the scope for further detailed information regarding the component acids of fats from all parts of plants. It is not beyond our province, it may be hoped, to point out that work of this nature is only useful when it is as quantitative as possible, when quantitative data are substantiated by careful evidence as to the individuality of at least the chief component acids, and, above all, when the identity of the species from which the fat is derived is known with certainty.

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CHAPTER V

THE COMPONENT GLYCERIDES OF NATURAL FATS: DATA OBTAINED MAINLY FROM QUALITATIVE INVESTIGATIONS

It was emphasised in the introductory Chapter I (p. 14) that the biological relationships which are so prominent when the composition of the component acids of natural fats are considered have no counterpart in the mode of combination of constituent acids into mixed triglycerides; that the fatty acids, in fact, seem to be woven into molecules of mixed triglycerides on the same general principle, whatever their place of origin may be—vegetable or animal, depot (reserve) or tissue (organ) fat—and whatever may be the particular nature of acids present as component fatty acids. This circumstance renders unnecessary, perhaps, adherence to the sequence followed in the three previous chapters devoted to the discussion of the component acids of fats from aquatic sources, land fauna, and land flora. At all events, in the present state of our knowledge, the presentation of the evidence will be made more clear if it follows the chronological sequence of investigations of glyceride structure. Until about 1927, such studies were for the most part of a qualitative character; but the consensus of results pointed unmistakably to the prevalence in nature of mixed rather than simple triglycerides. The quantitative investigations made since 1927 have, as already mentioned in Chapter I, confirmed and amplified these conclusions. They have been concerned very largely with vegetable seed fats, in which the characteristic "evenly distributed" type of glyceride structure is usually remarkably well defined; whilst modified forms of this structure have been observed in some other fats, notably depot fats and milk fats of the larger herbivorous mammals.

It is therefore convenient to discuss the component glycerides of natural fats as follows:

(*a*) The earlier, mainly qualitative, studies prior to 1927, which form the subject of the present chapter;
(*b*) The component glycerides of vegetable fats (Chapter VI);
(*c*) The component glycerides of animal fats (Chapter VII).

For what seems an unnecessarily long time after Chevreul had discovered in 1823 that the natural fats were glycerol esters of palmitic, stearic, oleic, and other acids, it was more or less tacitly assumed that they were necessarily mixtures of *simple* triglycerides such as tripalmitin, tristearin, triolein in varying proportions; although in 1860, when the trihydroxylic structure of glycerol had become recognised, Berthelot[1] had pointed out the possibility that fats might contain mixed triglycerides.

This is somewhat amusingly illustrated by an incident which occurred only about fifty years ago. In 1897 Heise[2] announced that mkanyi (*Allanblackia Stuhlmannii*) fat yielded by simple crystallisation from an appropriate solvent considerable amounts of an oleodistearin, and Henriques and Künne,[3] in view of what they termed this "unusual" observation, repeated the work and confirmed his conclusions. A very few years later, the work of Klimont, Bömer, and others on the resolution of fats by systematic crystallisation from different media presented ample, if somewhat negative, evidence that the vast majority of natural fats do *not* contain any significant amount of simple triglycerides, and at the present time it would be considered very "unusual" if a seed fat of the fatty acid composition of that of *Allanblackia* (*cf.* p. 264) were found to contain any quantity of a simple triglyceride.

It is rather unfortunate, although consistent with the curious neglect which many organic chemists have accorded to the fats as a class, that the "tripalmitin-tristearin-triolein" complex is still presented to the elementary student of the present day in the pages of a few otherwise accurately informed text-books of organic chemistry and also chemical physiology ; at any time in the past quarter of a century the case could more accurately, and quite safely, have been put as Leathes and Raper [4] express it : "the probability is that as a rule they" (glycerides in natural products) "are mixed."

FRACTIONAL CRYSTALLISATION OF SOLID NATURAL FATS

In 1901 Holde and Stange [5] separated the solid fractions deposited from a solution of olive oil in ether at —40° and recrystallised them from ether-alcohol at —40° and subsequently at 0°. They thus obtained a mixture of solid glycerides which melted at 30–31° and had an iodine value of 29·8 and saponification value of 196. The saturated acids present in this fraction melted at 52–61° (mean molecular weight 265·4) and the unsaturated acids had an iodine value of 90·0 (mean molecular weight 282). This corresponds with a molecular ratio of almost exactly two parts of saturated to one part of unsaturated.

In 1902 Fritzweiler [6] crystallised cacao butter from chloroform and ether-alcohol and obtained 6 per cent. of a glyceride (m.p. 44·5–45°) which he identified as oleodistearin. The same glyceride together with oleodipalmitin (m.p. 37–38°) was also isolated in small quantities from this fat by Klimont, who used acetone-chloroform and alcohol-ether as solvents [7] ; at first he also reported the presence of oleopalmitostearin, but withdrew this statement later, although in the light of modern work it may well be that it was well-founded. Klimont also isolated apparently the same oleodistearin and oleodipalmitin from Borneo tallow [8] and stillingia ("Chinese vegetable") tallow [9] and considered that the similarity between all three fats in texture and other physical properties was due to the presence in each case of considerable quantities of oleodistearin and oleodipalmitin. From the fact that removal of a solid fraction by crystallisation left a dissolved residue not markedly higher in iodine value than the original fat, he also deduced that triolein was not present to any considerable extent.

In 1909 Klimont [10] isolated stearodipalmitin, m.p. 59–60°, from duck fat and from goose fat and proved that triolein was also present in duck fat ; and in 1912 he [11] similarly showed that the simple triglyceride tripalmitin (m.p. 61·5°) could be isolated by fractional crystallisation from rabbit fat.

From about 1907 onwards Bömer and his co-workers were occupied with similar systematic crystallisations of various animal and vegetable fats ; in Bömer's hands the method was elaborated to an extraordinary degree, and in some cases many hundreds of crystallisations were involved in the examination of a single fat. Although in many cases the quantitative results obtained were perhaps hardly a recompense for the enormous amount of tedious manipulation which must have been involved, they served to prove that the natural fats were built up for the most part of mixed glycerides, and that the old conception of fats as mixtures of simple triglycerides was in no case even approached ; moreover, in some cases, it was found possible to give an approximate estimate of the amount of some of the higher melting and more sparingly soluble components present.

Thus, in the case of mutton tallow,[12] the isolation of 3 per cent. of tristearin, and 4–5 per cent. of dipalmitostearin (m.p. 57·5°) with palmitodistearin (m.p. 63·6°) was achieved (Hansen [13] and Kreis and Hafner [14] had previously obtained palmitodistearins from mutton and also from beef tallow). Bömer [15] also isolated 3 per cent. of palmitodistearin (m.p. 68°) and 2 per cent. of dipalmitostearin (m.p. 58°) from lard, whilst Amberger and Wiesehahn,[16] in another investigation of lard in 1923, observed the same proportions of these components, together with 2 per cent. of oleodistearin (m.p. 42°), 11 per cent. of oleopalmitostearin (m.p. 41°) and 82 per cent. of an oil which they believed to consist mainly of palmitodiolein.

Further applications of the direct fractional crystallisation of solid animal fats are the study of butter fat by Amberger [17] and further examinations of goose fat (*cf.* Klimont, p. 225) by Amberger and Bromig [18] and by Bömer.[19] Amberger isolated small quantities of palmitodistearin, dipalmitostearin, oleodipalmitin, and butyropalmito-olein from butter fat and also indicated that about 2 per cent. of triolein and some butyrodiolein were possibly present. In goose fat Amberger and Bromig detected dipalmitostearin, oleodipalmitin, palmitodiolein, and possibly triolein, whilst Bömer's results led him to suggest that its probable composition was triolein about 45, palmitodiolein about 30, stearodiolein about 5, dipalmitostearin (m.p. 57·6°) 3–4 per cent., and a very small amount of palmitodistearin (m.p. 63·5°) ; except in the cases of the palmitostearins, the numerical percentages quoted are probably only a rough indication of the actual amount of the individual components.

In 1920, with Baumann,[20] Bömer studied coconut fat, from which he failed to isolate any trilaurin, but obtained evidence of the presence of much dilauromyristin (m.p. 33°) with smaller amounts of laurodimyristin (m.p. 38°) and dimyristopalmitin (m.p. 45°), traces of dipalmitostearin (m.p. 55°) and a considerable quantity of a most-soluble fraction (m.p. 15°) which he believed to be caprolauromyristin (but which the more recent work would indicate to be a complex mixture of the still unresolved more soluble components of the fat). In 1924 Bömer and Schneider [21] published similar results for palm kernel fat, again finding considerable amounts of dilauromyristin (m.p. 33°), with less laurodimyristin (m.p. 40°), dimyristopalmitin (m.p. 45°), and myristodipalmitin (m.p. 51°) and, again, no evidence of trilaurin ; the greater part of the fat remained as a most-soluble residue (m.p. 14°) which these workers believed to be capromyristo-olein (this conclusion again, in view of later work, was probably not well-founded). Finally, in 1928, Bömer and Ebach [22] demonstrated that when trilaurin or trimyristin is present in appreciable quantity in a fat, isolation by their crystallisation procedure presents no difficulty, since they obtained about 30 per cent. of trilaurin from the seed fat of *Laurus nobilis* and about 40 per cent. of trimyristin from nutmeg butter. Bömer's last study [23] of this kind, published posthumously in 1938, dealt with the similar distillation and fractional crystallisation of the glycerides of babassu fat, another Palmæ seed fat which was shown to contain much dilauromyristin, some quantity of laurodimyristin, and small amounts of dimyristopalmitin.

The presence in nutmeg butter and laurel kernel oil of large proportions of simple triglycerides such as trimyristin and trilaurin, and the occurrence of small proportions of tripalmitin in certain fats, notably olive oil, palm oil or rabbit fat, may seem at first sight to make the glyceride structure of natural fats still more confused and bewildering. In nearly all cases in which simple triglycerides have been observed, however, it soon becomes clear that their presence is a secondary effect conditioned by the predominance of a particular saturated fatty acid in the fat in question. Thus the principle of " even distribution " operates almost to the full limits in the case of nutmeg butter ; but, since myristic acid forms about 75 per cent. of the total component acids of this fat, it necessarily follows that a considerable amount of this must be present as trimyristin, over and above the portion present in association with the other acids (oleic, etc.) in the form of mixed myristo-glycerides. Again, in instances where palmitic is practically the only saturated acid present, and in which the proportion of fully saturated glycerides, although small, is somewhat higher than if the saturated and unsaturated acids were completely distributed as mixed saturated-unsaturated glycerides, the fully saturated components are perforce essentially tripalmitin ; this accounts for the presence of the latter in small quantities in olive or palm oils, etc.

Prior to Bömer's studies, Krafft [24] had separated trilaurin from laurel kernel fat, and trimyristin from nutmeg butter, by partial distillation of the fats in a high vacuum. Similarly, Caldwell and Hurtley [25] had attempted to isolate some of the supposed simpler glycerides present in coconut fat or in butter fat by partial fractional distillation of these fats in the vacuum of the cathode light. In his work on coconut and babassu fats, and also on laurel kernel fat and nutmeg butter, Bömer [20, 22, 23] also employed partial distillation in a vacuum as a means of separating the constituents of smallest molecular size. In this way he was able to obtain distillates which contained considerable amounts of the mixed glycerides of lower molecular weight (lauromyristins, and so forth) which were present in the original fats. This procedure facilitated the subsequent application of the fractional crystallisation procedure, and indicates a useful extension in the technique of these methods. With the pressures available, it was not possible to distil without decomposition the mixed glycerides of average equivalent about 280 or above containing oleic or linoleic acids as part of the molecule.

It appears from more recent work published by other investigators (*cf.* p. 244) that evaporation of natural fatty glycerides at the very low pressure of the " molecular still," whilst affording some separation of mixed glycerides, does not lead to anything approaching a complete separation of such frequent components of fats as, for instance, oleopalmitostearin and palmitodiolein. On the other hand, crystallisation of solid or liquid fats from acetone (at moderate or very low temperatures according to circumstances) has become a most useful method of resolving fats into mixtures, of less complexity than the original fat, which are more amenable than the latter to quantitative examination (see Chapter VI, pp. 241, 244).

FRACTIONAL CRYSTALLISATION OF COMPLETELY HYDROGENATED FATS

In 1920 Amberger [26] submitted completely hydrogenated rape seed oil to fractional crystallisation and isolated stearodibehenin in quantity, thus indicating the presence of corresponding amounts of oleodierucin in the original fat; in 1924, with Bauch,[27] he made a similar examination of hydrogenated cacao butter and of the original fat, from which it was suggested that the latter contained traces of tristearin and β-palmito-αα′-distearin, 25 per cent. of oleo-αβ-distearin, 20 per cent. of β-palmito-oleo-stearin and 55 per cent. of α-palmitodiolein, but these figures do not agree in all respects with the most recent results (*cf.* Chapter VI, p. 262).

Bömer and Engel [28] fractionally crystallised hydrogenated chaulmoogra oil and isolated 79 per cent. of dihydrochaulmoogro-didihydrohydnocarpin and 13 per cent. of dihydrohydnocarpo-didihydrochaulmoogrin; the component fatty acids of the fat contained 40 per cent. of chaulmoogric and 59 per cent. of hydnocarpic acids and consequently the observed mixed glyceride composition conforms closely with that which would be expected from the general results obtained by the quantitative investigations of the constitution of seed fats (*cf.* Chapter VI, pp. 233–236).

The examination of partially or completely hydrogenated fats (with reference to the amount and component acids of the fully saturated glycerides produced in the former case, or to the proportions of tristearin present in the completely hydrogenated products) has also been carried out in many cases in connection with the quantitative studies which are discussed at some length in Chapters VI and VII. This method of examination will accordingly receive further attention in the succeeding chapters.

FRACTIONAL CRYSTALLISATION OF BROMINATED GLYCERIDES FROM LIQUID FATS

A modification of the crystallisation method has also been adopted with some success, namely, the bromination of unsaturated fats in light petroleum, followed by isolation of various individual bromo-glycerides by crystallisation from various solvents. This procedure which, like those already mentioned, gives results mainly qualitative in character, has thrown considerable light on the types of glycerides present in a wide variety of drying oils.

In the important case of linseed oil, Eibner,[29] with Widenmayer, Schild, and Brosel, isolated the bromo-adducts of α-linoleo-di-α-linolenin, β-linoleo-di-α-linolenin (m.p. 143–144°), and oleo-dilinolenin (m.p. 72–73·5°). Eibner suggested that the last-named may account for all the oleic acid in the oil, whilst linoleo-dilinolenin is probably the chief drying principle; he also pointed out the probability that all oleic acid present is linked with linoleic or linolenic acids, thus disposing of the view that its presence in linseed oil is necessarily a deterrent to the drying qualities.

Suzuki and Yokoyama [30] also reported the isolation from linseed oil of brominated glycerides derived from a dilinoleo-linolenin, two linoleo-dilinolenins, two linoleo-dioleins, an oleodilinolein, oleo-linoleo-stearin and oleo-linoleno-stearin; whilst in soya bean oil they have similarly obtained evidence of the presence of dilinoleo-linolenin, linoleo-dilinolenin, oleo-dilinolein, linoleo-diolein, and oleo-linoleno-stearin. Hashi [31] arrived at similar conclusions, identifying in addition the presence of oleodipalmitin and oleo-dilinolein. Simple triglycerides were not reported.

Suzuki and Masuda [32] applied the fractional crystallisation process of brominated glycerides to marine animal oils, including whale oil and cod liver, herring, sardine, salmon, shark liver, sand eel, and cuttlefish oils. In all these cases the results disclosed a most complex mixture of unsaturated glycerides (ten or more different bromo-derivatives having been isolated from some of the fats); hexadecenoic, oleic, linoleic, and the unsaturated acids of the C_{20} and C_{22} series are linked, two or three at a time, in numerous combinations, but simple triglycerides appear to be absent.

The evidence obtained by those, especially Bömer, Klimont, and Amberger, who devoted such painstaking study to the simple fractional crystallisation of solid fats points unmistakably to the substantial absence of simple triglycerides from any of the fats they studied, with the sole exceptions of laurel oil and nutmeg butter (which must be regarded, for reasons already stated, as special cases).

The whole of the investigations referred to above—whether of natural solid fats, of hydrogenated natural fats, or of the bromo-additive products of natural fats—were based essentially upon attempted separation of triglycerides by the physical method of crystallisation. The results obtained were almost wholly qualitative in character, and in only a few instances led to even an approximate statement of the proportion of any individual mixed triglyceride present. Nevertheless they are in themselves sufficient to demonstrate conclusively the generalisation that seed fats are mixtures of mixed triglycerides, and that the occurrence of simple triglycerides is quite exceptional.

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CHAPTER VI

THE COMPONENT GLYCERIDES OF VEGETABLE FATS

FROM about 1927 onwards, more definitely chemical methods of attack upon the problem of glyceride structure have been employed in place of or in conjunction with the partial separation of triglycerides by crystallisation from solvents. These methods, developed for the most part at the University of Liverpool by the writer and his collaborators, usually lead to more or less quantitative statements of the different component glycerides present in natural fats, or at least define the limiting proportions of different groups of component glycerides. In a number of instances it has now become possible to give approximate figures for the proportions of each of the main component mixed glycerides present in natural fats, whilst in a few cases the configuration of individual mixed glycerides such as, for example, β-oleodistearin or β-palmito-oleostearin can be stated with some confidence. Both vegetable (seed and fruit-coat) and animal (depot and milk) fats have been studied quantitatively or semi-quantitatively by these methods; the number of fats so investigated naturally falls far short of that of the fats whose component acids have been quantitatively determined (Chapters II, III, and IV), but is sufficient to define clearly the modifications in glyceride structure which are characteristic of different groups of natural fats. In the present chapter the information obtained by the more recent methods regarding the component glycerides of seed fats and fruit-coat fats will be considered, first from a general standpoint, and subsequently with reference to the more important fats in each of the two groups.

The modern methods of investigation have evolved somewhat as follows:

I. Determination of the proportion of fully saturated glycerides present in natural fats.

II. Determination of the tri-unsaturated C_{18} glycerides (oleic+linoleic, etc.) in liquid fats:

- (*a*) By estimation of the tristearin content of the completely hydrogenated fat;
- (*b*) By study of the glyceride composition of the fat after hydrogenation to varying extent.

III. (*a*) More detailed examination of the component glycerides in solid seed or animal fats by separating the latter into fractions varying in solubility in acetone, each fraction being examined separately for its fatty acid composition, fully saturated glyceride content, content of tri-unsaturated C_{18} glycerides, etc.

(*b*) Similar examination of liquid vegetable or animal fats by systematic crystallisation from acetone at suitable temperatures down to −60°, each fraction being then examined separately for its fatty acid composition.

Method I has led to full confirmation of the tendency to mixed glyceride formation revealed by the physical studies of previous investigators (*cf.*

Chapter V), and to the generalisation that the fatty acids are distributed in general remarkably evenly and widely amongst the glycerol molecules. In the liquid fats in which oleic and other unsaturated acids predominate, the absence of fully saturated glycerides merely establishes one aspect of this "even distribution," but the application of methods II (*a*) or (*b*) to these cases has shown that the proportion of tri-unsaturated C_{18} glycerides is uniformly much closer to the lowest possible than to the highest possible values (calculated from the fatty acid compositions), thus again establishing a maximum degree of association between saturated and unsaturated acids in the form of mixed saturated-unsaturated triglycerides. Finally, preliminary resolution of some of the simpler fats by crystallisation from acetone at 0° into fractions in which either fully-saturated, mono-oleo-disaturated, or dioleo-monosaturated glycerides respectively predominate (method III (*a*)) has permitted detailed quantitative statements to be given for the proportions of at least the major component mixed glycerides present. The compositions thus arrived at experimentally are not far removed from those which can be deduced from certain simple arithmetical considerations from the *composition of the total fatty acids* in these fats, and it would appear that, so long as a fat containing only three or four major component acids is known to be assembled on the lines of what has been termed "even distribution," the proportions of the chief mixed glycerides present may be capable of prediction within approximate limits without recourse to the lengthy experimental determination of its glyceride structure.

DETERMINATION OF THE FULLY SATURATED GLYCERIDE CONTENT OF A FAT *

In 1927 Hilditch and Lea [1] showed that when a fat is oxidised in acetone solution with powdered potassium permanganate all glycerides containing one or more unsaturated acyl radicals are ultimately converted into the corresponding azelao-glycerides (in the case of oleo-, linoleo-, linoleno- or elæostearo-glycerides), whilst the completely saturated glycerides remain unattacked. If the possible combinations of glycerol with a saturated fatty acid ($S.CO_2H$) and an unsaturated (e.g. oleic) acid ($U.CO_2H$) be considered, it will be seen that the following products may arise :

	ORIGINAL GLYCERIDE	GLYCERIDE PRODUCT OF OXIDATION
Fully saturated	$C_3H_5(O.CO.S)_3$	$C_3H_5(O.CO.S)_3$
Mono-oleo-derivative	$C_3H_5<\substack{(O.CO.S)_2 \\ (O.CO.U)}$	$C_3H_5<\substack{(O.CO.S)_2 \\ (O.CO.[CH_2]_7.CO_2H)}$
Dioleo-derivative	$C_3H_5<\substack{(O.CO.S) \\ (O.CO.U)_2}$	$C_3H_5<\substack{(O.CO.S) \\ (O.CO.[CH_2]_7.CO_2H)_2}$
Triolein	$C_3H_5(O.CO.U)_3$	$C_3H_5(O.CO.[CH_2]_7.CO_2H)_3$

The acid azelaic glycerides usually form a complex mixture which is somewhat difficult to separate from the unchanged fully saturated glycerides, because the alkali salts of the azelao-glycerides are very strong emulsifying agents (especially those of the monoazelao-derivatives, which in addition are soluble in ether as well as in water). By taking suitable precautions during the removal of the acid azelao-glycerides by washing with alkali it is, however, quite possible to recover quantitatively the unchanged fully saturated glycerides.

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* For details of the experimental technique used in the study of glyceride structure, see Chapter XI, pp. 513–526.

If the component glycerides of a fat are considered with respect to the two groups of fatty acids, saturated (S) and unsaturated (U), it is evident that the following types of triglyceride (G=glyceryl residue) may be present:

$$GS_3, GS_2U, GSU_2, GU_3$$

The proportion of fully saturated glycerides (GS_3) leaves three possible group components to be estimated. If the component acids of the original fat and of the fully saturated portion are known, the amounts of the saturated acids linked in mixed glycerides with unsaturated acids can be deduced. This (molecular) " association ratio," as it has been termed, of saturated to unsaturated acids in the non-fully saturated portion of the fat permits the proportions of any two of the groups GS_2U, GSU_2, GU_3 to be calculated if one of them is absent or its amount known; or, alternatively, indicates limiting values between which the content of each of these groups must lie.

In the communication referred to, Hilditch and Lea [1] stated that cottonseed oil, with 25 per cent. of saturated acids in its total fatty acids, contained negligible amounts of fully saturated glycerides; and that the respective fully saturated glyceride contents of cacao butter and a specimen of mutton tallow * were 2 per cent. and 26 per cent., although their component fatty acids were very similar, namely, about 25 per cent. palmitic, 35 per cent. stearic and 40 per cent. oleic (including 1–2 per cent. of linoleic) acids.

Similar studies of coconut and palm kernel oils, and of other seed fats of high total saturated acid content, were next made by Collin and Hilditch [2, 3]; out of a total number of eleven seed fats examined, all but two † conformed with the " rule of even distribution " in that fully saturated glycerides did not appear in quantity unless the proportion of saturated acids in the total fatty acids exceeded about 60–65 per cent. Since then, the fully saturated glyceride contents of many other seed and fruit-coat fats have been determined, and no further marked exceptions to the general rule enunciated have been found. The results of most of these studies are expressed graphically in Fig. 2, and a summary of the quantitative data on which the graph is based is given in Table 62.

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* The much higher content of fully saturated components (relative to the proportion of saturated acids in the total acids of the whole fat) in the case of the sheep depot fat was subsequently found to be characteristic for the depot fats, and also for the milk fats, of most of the common herbivorous mammals (oxen, buffalo, sheep, pigs, goats). These represent special cases of glyceride structure which form a distinct group by themselves, as will be seen in Chapter VII. It may, however, be pointed out here that they represent a particular development of the general lines of glyceride structure which appear to operate throughout natural fats, and are not in any sense contradictory thereto. For instance, in spite of the frequently high proportion in such fats of fully saturated glycerides, the latter are almost wholly still of the mixed type, e.g. palmitostearins, and simple triglycerides such as tripalmitin or tristearin are almost completely absent.

† The exceptions were the seed fats of *Laurus nobilis* and *Myristica malabarica*. The latter is also exceptional in its content of resin acids, some of which appear to be in combination with glycerol. In laurel oil, the abnormally high quantity of fully saturated components is substantially trilaurin, and the remainder of the acids present (chiefly palmitic and oleic) appear to be " evenly distributed " in the usual manner.

TABLE 62

Number on Fig. 2	Species	Fat	Saturated Acids in Total Fatty Acids Per Cent. (Mol.)	Fully-Saturated Glycerides Per Cent. (Mol.)	"Association Ratio" * in Mixed Saturated-unsaturated Glycerides
		SEED FATS			
1	*Cocos nucifera*	Coconut oil	93·9	86	1·3–1·4
2	,, ,,	,, ,,	92·9	84	1·4
3	*Irvingia Barteri*	Dika fat	91·7	81	1·3
4	*Manicaria saccifera*	—	91·6	82	1·2
5	*Myristica fragrans*	Nutmeg butter	90·2	73	1·6
6	*Astrocaryum Tucuma*	Tucuma fat	88·0	73	1·25
7	*Acrocomia sclerocarpa*	Gru-gru fat	86·3	69	1·3
8	*Elæis guineensis*	Palm kernel oil	85·3	66	1·3–1·4
9	*Shorea stenoptera*	Borneo tallow	62·9	5·1	1·6
10	,, ,,	,, ,,	62·8	4·5	1·5
11	*Madhuca butyracea*	Phulwara butter	62·4	8	1·4
12	*Palaquium oblongifolium*	Taban Merah fat	60·2	1·8	1·5
13	*Theobroma cacao*	Cacao butter	59·8	2·5	1·4
14	*Garcinia indica*	Kokum butter	59·0	1·5	1·4
15	*Myristica malabarica*	—	59·2	19	1·0
16	,, ,,	—	56·2	16	1·0
17	*Laurus nobilis*	Laurel kernel	58·5	40·5	0·4
18	*Allanblackia Stuhlmannii*	Mkanwi fat	55·6	1·5	1·2
19	*Nephelium mutabile*	Pulasan fat	55·3	1·5	1·2
20	*Dacryodes rostrata*	Java almond fat	53·4	1·8	1·1
21	*Caryocar villosum*	Piqui-a	53·1	2·5	1·1
22	*Pentadesma butyracea*	—	51·6	3·0	1·0
23	*Garcinia morella*	Gamboge butter	50·5	2·7	1·0
24	,, ,,	,, ,,	49·4	2·0	0·9
25	*Nephelium lappaceum*	Rambutan fat	49·0	1·4	0·9
26	*Hodgsonia capniocarpa*	—	47·8	2·7	0·9
27	*Butyrospermum Parkii*	Shea fat	46·3	4·5	0·8
28	,, ,,	,, ,,	45·1	2·5	0·8
29	*Madhuca latifolia*	Mowrah fat	43·4	1·2	0·8
30	*Schleichera trijuga*	Kusum fat	34·6	1·2	0·6
31	*Azadirachta indica*	Neem oil	32·0	0·6	0·6
32	*Gossypium hirsutum*	Cottonseed oil	27·3	less than 1	0·3
33	*Arachis hypogæa*	Groundnut oil	15·5	,, ,, 1	0·2
34	*Sesamum indicum*	Sesamé oil	14·9	,, ,, 1	0·2
35	*Thea sinensis*	Teaseed oil	10·0	,, ,, 1	0·1
36	*Brassica campestris*	Rape oil	3·6	,, ,, 1	—
		FRUIT-COAT FATS			
a	*Stillingia sebifera*	Stillingia tallow	72·5	28·4	1·6
b	,, ,,	,, ,,	68·4	23·9	1·4
c	*Elæis guineensis*	Palm oil, Belgian Congo.	50·9	10·3	0·8
d	,, ,,	Palm oil, Sumatra.	51·2	2·0	1·0
e	,, ,,	Palm oil, Belgian Congo.	49·6	6·5	0·8
f	,, ,,	Palm oil, Malay	49·2	9·5	0·8
g	,, ,,	Palm oil, Cameroons.	49·1	8·3	0·8
h	,, ,,	Palm oil, Drewin.	46·6	7·4	0·7
i	,, ,,	Palm oil, Cape Palmas.	41·5	3·4	0·7
j	*Caryocar villosum*	Piqui-a Pericarp	45·9	2·3	0·8
k	*Dacryodes rostrata*	Pericarp	38·7	1·0	0·6
l	*Laurus nobilis*	Laurel berry	25·4	3·0	0·3
m	*Olea europæa*	Olive oil	13·8	2·0	0·1

* "Association ratio": Mols. saturated acid associated with one mol. unsaturated acid in mixed saturated-unsaturated glycerides.

It will be seen from Fig. 2 and Table 62 that, until the saturated acids in a seed fat amount to about 60 per cent. of the total fatty acids, the proportion of fully saturated triglycerides is insignificant. It so happens that there are few seed fats in which saturated acids form between 60 and 80 per cent. of the total fatty acids, but eight examples have been studied in which these form from 85–94 per cent. of the total acids. In each of these cases the proportion of fully saturated glycerides is large, but at the same time it is such that the molar ratio of saturated to unsaturated acids in the mixed saturated-unsaturated part of the fat is approximately constant at about

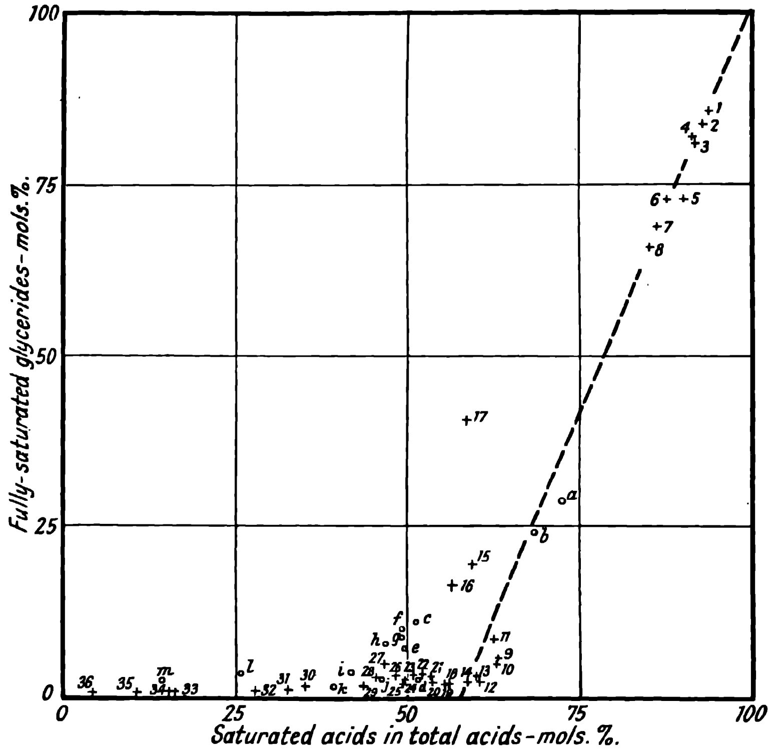

FIG. 2.

1·3 or 1·4 to 1. In other words, in the mixed saturated-unsaturated glycerides the saturated acids amount to nearly 60 per cent., or slightly less, of the mixed fatty acids present in this part of the fat. In Fig. 2, the broken line represents the relationship between the fully saturated glyceride content and the proportion of saturated to unsaturated acids in the whole fat which would obtain if the acids were distributed (when the proportion of saturated acids exceeds about 58 per cent.) so that as great an amount as possible of the triglycerides contained an average proportion of 1·4 mols. of saturated to 1 mol. of unsaturated acid in combination, the excess above this ratio of saturated acids appearing, of course, in the form of fully saturated triglycerides. (This ratio corresponds with a mixture of about 3–4 mols. of mono-unsaturated-disaturated glycerides with 1 mol. of di-unsaturated-mono-saturated glycerides.)

The general regularity with which the experimental findings approximate to this relationship in the seed fats indicates the strikingly uniform manner in which the constituent acids are assembled in these natural triglycerides, and also illustrates very well the operation of what has come to be termed the " rule of even distribution " in glyceride structure.

In the fruit-coat (pericarp, etc.) fats the generalisation appears not to hold so completely as in the seed fats. In the fruit-coat or pericarp fats of *Caryocar* and *Stillingia* the data accord exactly with the " even distribution " rule, but in olive, laurel berry, and palm oils there is usually a somewhat higher content of fully saturated triglycerides (in these cases tripalmitin, since palmitic forms almost the whole of the saturated acids present) than is consistent with the operation of this principle to the extent usually observed in the seed fats. On the other hand, as will be seen later, the remainder (i.e. the mixed saturated-unsaturated part) of these fats appears to be assembled on the usual lines. Relatively few examples of fruit-coat fats have yet been available for study, and it is hardly possible to say, on the evidence at present to hand, whether the strictly " evenly distributed " type is more common, or not, in this group of vegetable fats.

It has already been said that glyceride structure appears to be quite independent of the particular acids which are present. This is particularly well shown by the seed fats quoted in Table 62 which contain from 43 to 63 per cent. of saturated acids in the total fatty acids, and which also, it so happens, include several different saturated acids amongst their major component acids. It is therefore interesting to consider these fats in somewhat greater detail (Table 63).

TABLE 63

SEED FAT	COMPONENT SATURATED ACIDS PER CENT. (MOL.)				SATURATED ACIDS IN TOTAL ACIDS PER CENT. (MOL.)	FULLY-SATURATED GLYCERIDES IN FAT PER CENT. (MOL.)
	C_{14}	C_{16}	C_{18}	C_{20}		
Borneo tallow	—	19·5	42·4	1·0	62·9	5·1
" "	1·8	23·3	37·5	—	62·8	4·5
Phulwara butter	1·6	57·4	3·4	—	62·4	8·0
Palaquium oblongifolium	0·2	6·5	53·5	—	60·2	1·8
Cacao butter	—	24·3	35·5	—	59·8	2·5
Allanblackia Stuhlmannii	—	3·4	52·2	—	55·6	1·5
Nephelium mutabile	—	3·3	31·4	20·6	55·3	1·5
Dacryodes rostrata	—	11·7	39·8	1·9	53·4	1·8
Caryocar villosum	1·6	50·7	0·8	—	53·1	2·5
Pentadesma butyracea	—	5·9	45·7	—	51·6	3·0
Nephelium lappaceum	—	2·3	14·2	32·5	49·0	1·4
Shea butter	—	6·3	40·0	—	46·3	4·5
" "	—	9·3	35·4	—	45·1	2·5
Mowrah fat	—	24·1	19·3	—	43·4	1·2

In the group of fats illustrated in Table 63, the amount of fully saturated glycerides is for the most part insignificant, irrespective of whether the 43–63 per cent. of saturated acids in the whole fat consists very largely of one acid (either palmitic or stearic), or of a mixture of two saturated acids in quantity (either palmitic and stearic, or stearic and arachidic). Similarly, of the fats numbered 1–8 in Table 62 (which conform to the same generalisation, since their fully saturated glycerides represent the saturated fatty acids in excess of the amount necessary to give the approximately constant ratio of about 1·4 mols. of saturated per mol. of unsaturated acids combined together as mixed glycerides), the predominating saturated acids are lauric (45–50 per cent.) and myristic (about 20 per cent.) in the Palmæ seed fats (Nos. 1, 2, 4, 6, 7, 8), myristic (about 75 per cent.) in nutmeg fat, and myristic and palmitic in dika fat.

The general picture of glyceride structure exhibited by the relatively more saturated seed fats is thus that fully saturated glycerides do not appear in appreciable amounts until the saturated acids exceed about 60 per cent. or so of the total fatty acids. Put in the converse manner, so long as the unsaturated acids form somewhat more than one-third of the total fatty acids, at least one oleic group occurs in nearly every triglyceride molecule, *i.e.*, the amount of fully saturated glycerides is negligible. This exemplifies the " rule of even (or widest) distribution " as defined in Chapter I (p. 15).

It should be noted that formation of mixed glycerides by a process of *random distribution* of fatty acids amongst the triglyceride molecules would lead to quite different amounts of fully saturated glycerides in fats in which saturated acids form from about 30 to 70 per cent. of the total fatty acids. With " random " distribution, the amount of fully saturated triglycerides would be proportional to the cube of the proportion of saturated acids in the total fatty acids: with 50 per cent. saturated acids the amount of fully saturated glycerides would be 12·5 per cent. of the fat, with 63 per cent. of saturated acids it would reach 25 per cent. (whereas in " evenly-distributed " fats fully saturated glycerides are still negligible at this fatty acid composition).

Naturally, at the extreme ranges of the fatty acid composition curve (*e.g.*, below about 20 per cent., and above about 80 per cent., of saturated acids), the proportions of fully saturated glycerides are much the same, and often within the limits of experimental error of determination of the fully saturated glyceride content, for both the " even " and the " random " type of fatty acid distribution.*

Bhattacharya and Hilditch[9] drew attention to these characteristic differences between " even " and " random " distribution in glyceride structure in 1930, soon after the general existence of " even distribution " in seed and other natural fats had been established. These authors showed at the same time that, when mixed glycerides are synthesised *in vitro* by heating mixtures of fatty acids with glycerol in a vacuum, the fatty acids combine with the glycerol in a manner which very closely, but not wholly, approaches to "random" distribution—in marked contrast to the "even" or "widest" distribution observed in most natural fats.

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* Owing to this coincidence, Jackson and Longenecker[10] have indeed suggested that babassu fat (a Palmæ seed fat with 86·7 per cent. of saturated acids in its total acids, and with 67·3 per cent. of fully saturated glycerides) is constituted on a plan of " random " distribution. Whilst it is true that the amount of fully saturated glycerides proportional to the cube of 86·7 is 65·2 per cent., the amount corresponding to this proportion of saturated acids, read from the " even distribution " graph in figure 2, is 70 per cent.—the observed figure being 67·3 per cent.

The explanation in terms of " even distribution," which covers the whole range of mixtures of saturated and unsaturated acids, is clearly more generalised and logical than the assumption that " even distribution " holds merely over the range in which its effects happen to be analytically distinguishable from those of " random " or " indiscriminate " distribution.

THE GENERAL GLYCERIDE STRUCTURE OF SEED FATS IN WHICH OLEIC AND LINOLEIC ACIDS ARE THE CHIEF COMPONENT ACIDS

There are, of course, a very large number of liquid seed fats in which the amount of saturated acids is relatively small. In these cases (of which the fats numbered 32–36 in Table 62 are typical instances) fully saturated glycerides are practically absent or, at least, present in exceedingly small proportions. Whilst this indicates the usual tendency towards "even distribution," in so far as the minor amounts of saturated acids in these liquid fats are thereby shown to be almost wholly present in the form of mixed saturated-unsaturated triglycerides, it does not furnish any direct information as to the composition of the latter. Other methods had therefore to be devised for this purpose.

The isolation of various crystalline mixed glycerides formed by addition of bromine to unsaturated fats had, as already mentioned, served in the hands of Eibner,[4] Suzuki [5] and their collaborators to give a qualitative demonstration of the presence of many mixed glycerides of oleic, linoleic, and linolenic or saturated acids in linseed oil and soya bean oil; but this procedure has so far not proved adaptable to even an approximately quantitative treatment.

Hilditch and co-workers [6] have been able to put forward a certain amount of general quantitative evidence by investigating the mixture of glycerides produced from liquid seed fats when completely or partly hydrogenated. In all the instances studied the unsaturated acids of the fats belonged practically exclusively to the C_{18} series (oleic, linoleic, linolenic), and of course hydrogenation methods (involving ultimately the determination of stearic glycerides) afford no evidence as to whether the unsaturated glycerides, finally determined in the form of stearic glycerides, were derived from oleic, linoleic, or linolenic acids. Nevertheless, two independent experimental methods have been worked out which lead to an approximate estimate of the triglycerides present in such fats in which all three acyl groups are those of C_{18} acids. Consequently, just as in the more saturated fats it has proved possible to obtain quantitative evidence of the distribution of the saturated acids, as a class, in contradistinction to the unsaturated acids, so it was found feasible to determine, at all events approximately, the content of triglycerides wholly made up of C_{18} acids in a number of liquid seed fats. Since the amount of stearic acid in the fats studied was extremely small, the results obtained represent, within near limits, the proportions of triglycerides made up wholly of unsaturated C_{18} acids which are present.

If X is the molar percentage of acids of the C_{18} series (almost entirely oleic and linoleic) in the total acids of a liquid seed fat of this type, and if $2y$ is the molar percentage of the saturated, non-C_{18} acids,* the proportion of mixed saturated-unsaturated glycerides must be either $3y$ or $6y$ (or between these limits), according as to whether there are two acyl groups of the non-C_{18}

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* Determination of the fully saturated glycerides either shows the latter to be absent, or permits allowance to be made for the small proportion of saturated acids which may be present in this form.

series associated with one of the (unsaturated) C_{18} series, or *vice versa*. The amount of triglycerides wholly made up of C_{18} acids ("tri-C_{18} glycerides") must therefore lie between the limits of $X-3y$ and $X-6y$ (mol. per cent. of the fat). Since, in the fats under consideration, the unsaturated C_{18} acids are greatly in excess of the saturated non-C_{18} acids, the principle of "even distribution" would result in the latter being mainly present as mono-saturated-di-unsaturated (C_{18}) glycerides, so that we should expect the amount of unsaturated C_{18} acids present in these mixed glycerides to be much nearer the maximum than the minimum. Correspondingly, the amount of tri-C_{18} glycerides would then be nearer the minimum ($X-6y$) than the maximum ($X-3y$).

One method of determining the content of tri-C_{18} glycerides in a fat consists [6] in completely hydrogenating a specimen of the fat and separating the product into a series of fractions by systematic crystallisation from anhydrous ether. Tristearin and palmitodistearin are thus concentrated into the least soluble fractions, and the proportion of tristearin in each can be approximately ascertained from the respective saponification equivalents of the fractions. Unfortunately, a certain amount of acyl migration may occur during hydrogenation of a fat at or above about 170° (the temperature employed in obtaining the data quoted below). This does not take place at lower temperatures, and in work of this nature hydrogenation should be effected as rapidly as possible at 100–120° (with Raney nickel, palladium or platinum as catalyst). The hydrogenation methods are thus open to some objection, and moreover the accurate determination, from the saponification equivalent, of tristearin in the mixtures of the latter with palmitodistearin obtained by crystallisation of the completely hydrogenated fats is not easy, owing to the relatively small difference (9·3) between the equivalents of palmitodistearin and tristearin.

The later methods of preliminary resolution of a fat by crystallisation from acetone (*cf.* pp. 241–244) have made it possible to dispense for the most part with the hydrogenation procedures, which are therefore only briefly discussed here.

The complete hydrogenation procedure was, however, applied [6a] to cottonseed, soya bean, and linseed oils with the results shown in Table 64A. In this table are included the possible limiting values for tri-C_{18} glycerides, derived from the component acids and the known absence of fully saturated glycerides, according to whether the non-C_{18} acids are associated with C_{18} acids in the ratio of two of the former to one of the latter, or conversely. It will be seen that, in each of the three oils studied by this method, the observed content of tri-C_{18} glycerides is close to the minimum possible, indicating close conformity with the "rule of even distribution."

TABLE 64A. *PROPORTION OF TRI-C_{18} (MAINLY OLEIC AND LINOLEIC) GLYCERIDES IN CERTAIN LIQUID SEED FATS*

SEED FAT	COMPONENT ACIDS PER CENT. (MOL.)			POSSIBLE LIMITS FOR TRI-C_{18} GLYCERIDES	TRI-C_{18} GLYCERIDES (ESTIMATED AS TRISTEARIN)
	NON-C_{18}†	STEARIC	UNSATURATED C_{18}	PER CENT. (MOL.)	PER CENT. (MOL.)
Cottonseed oil	25·4	1·7	72·9	24–62	24
Soya bean oil	8·4	5·7	85·9	75–87	75
Linseed oil	6·2	4·0	89·8	81–91	83

† Almost wholly palmitic acid.

An alternative method, probably less liable to experimental error but very tedious in execution, is to prepare a series of partly hydrogenated fats from the liquid seed fat and to determine the proportion of fully saturated glycerides, and the component acids present therein, for each partly hydrogenated fat. From the total component acids in the latter, and the data thus obtained, the proportion of each component acid in the non-fully saturated glycerides of each fat follows by difference. Now, it has been established[8] that in a fat in which disaturated-mono-unsaturated glycerides are present in relatively small quantities, these reach the state of complete saturation, during hydrogenation, before any originally monosaturated-di-unsaturated or tri-unsaturated glycerides become completely hydrogenated. There follows a period in which the remaining non-fully saturated glycerides consist of a mixture of glycerides corresponding with monosaturated(non-C_{18})-di-unsaturated(C_{18})-glycerides and tri-unsaturated(C_{18})—glycerides in the original fat; whilst at a later stage, and before all of the former have become completely hydrogenated (mono-non-C_{18}, di-C_{18}-saturated glycerides), tristearin commences also to appear in the fully saturated portion of the hydrogenated fat. If, therefore, the component acids of the mixed saturated-unsaturated glycerides of each partly hydrogenated fat are calculated in the form of a mixture of mono-(non-C_{18})-di-C_{18} glycerides with tri-C_{18} glycerides, the values obtained for the latter will be correct only over the second stage of the hydrogenation process referred to above. Over the whole series, therefore, the estimates of tri-C_{18} glyceride content will first rise to a maximum, then remain constant for a time, and finally again fall. These maximum values, which are usually in good agreement, represent the true content of tri-C_{18} (mainly oleic and linoleic) glycerides present in the original fat.

This method has been applied[6] to cottonseed, groundnut, sesamé, and teaseed oils, and the liquid fruit-coat fat olive oil with the results shown in Table 64B. In each fat the estimated tri-C_{18} glyceride content is close to the minimum possible value, again indicating the tendency to "even distribution," i.e. maximum production of mixed triglycerides.

TABLE 64B. *ESTIMATION OF TRI-C_{18} GLYCERIDES IN LIQUID VEGETABLE FATS BY PROGRESSIVE HYDROGENATION*

Fat	Component Acids Per Cent. (Mol.)			Possible Limits for Tri-C_{18} Glycerides Per Cent. (Mol.)	Maximum Tri-C_{18} Glycerides Observed Per Cent. (Mol.)
	Non-C_{18} †	Stearic	Unsaturated C_{18}		
Cottonseed	25·4	1·7	72·9	24–62	24–25
Groundnut	14·8	3·0	82·2	55·5–78	56·5–57
Sesamé	10·7	4·2	85·1	68–84	69
Teaseed	8·5	2·2	89·3	71–86	69
Olive (Tuscany)	13·0	2·8	84·2	65–82 *	64–65·5
,, (Palestine)	12·6	3·3	84·1	66–82 *	70

* After allowing for 2 per cent. fully saturated glycerides (tripalmitin).
† Mainly palmitic acid.

It is quite evident, from the data in Tables 64A and 64B, that the principle of "even distribution" of fatty acids in the mixed triglyceride molecules is as generally operative in seed fats in which oleic and linoleic acids predominate as in those more saturated fats in which high proportions of palmitic, stearic, and other saturated acids are present.

Morrell and Davis [11] have proved that a similar state of affairs holds in tung and oiticica oils, in which large proportions respectively of elæostearic acid and licanic (keto-elæostearic) acid occur. These acids contain a trebly conjugated system of ethenoid linkings and, as is well known, the naturally occurring (" α ") form of each acid or its glycerides is readily isomerised by the action of light or suitable catalysts into a geometrically-isomeric (" β ") form of higher melting point and sparing solubility. Morrell and Davis found that the isomerised, crystalline "β-elæostearin" from tung oil (in which elæostearic acid forms over 80 per cent. of the component acids) is almost pure tri-β-elæostearin ; on the other hand, the component acids of oiticica oil include only about 70 per cent. of licanic acid, and, correspondingly, these authors observed that the " β-licanin " similarly obtained by isomerisation of the oil contained but little tri-β-keto-elæostearin, but was chiefly a mixture of glycerides in which two keto-elæostearic groups were associated with one saturated, or non-conjugated unsaturated, acid group. This is a further example of the fact that glyceride structure is independent of the particular component acids which may be present in a seed fat.

MORE DETAILED DETERMINATION OF GLYCERIDE STRUCTURE IN SEED FATS

The most recent developments in this field are the determination, within approximate limits, of the proportions of each of the most abundant mixed glycerides present in fats derived from comparatively simple mixtures of acids (e.g. palmitic, stearic, oleic, and linoleic), together with the discovery of a formula by means of which the proportions of the major component glycerides in an " evenly distributed " fat can be roughly computed from the composition of the mixed fatty acids alone. The procedure involved was first applied to cacao butter, mowrah fat, shea butter, phulwara butter, Borneo tallow, and kepayang oil and has since been employed in many other cases. It depends on the fact that systematic crystallisation of such fats from acetone at suitable temperatures, although usually incapable (as earlier investigators found) of yielding definite individual mixed glycerides, affords with comparative ease a division of the fat into sparingly soluble portions in which mono-unsaturated-disaturated glycerides predominate, and more soluble portions in which the di-unsaturated glycerides (and tri-unsaturated glycerides when present) are concentrated.

The general principles which operate in the separation of the various groups of mixed glycerides by crystallisation from acetone are illustrated by Table 65. This indicates the four main types of glycerides (from fully saturated to completely unsaturated) and gives the range of melting points and some typical individual components of each group, together with a rough diagrammatic representation of the chief components present in hard solid, soft solid and liquid fats. It includes similar diagrammatic indications of the general composition of the various fractions into which a fat may be separated (i) in the cases of solid or semi-solid fats crystallised from acetone at not lower than 0° or —10°, and (ii) in liquid fats for which the temperatures employed in crystallisation from acetone may range from about 0° down to —40° or lower.

TABLE 65. *GENERAL SEPARATION OF COMPONENT GLYCERIDES EFFECTED BY CRYSTALLISATION FROM ACETONE*

TRIGLYCERIDES	Saturated Saturated Saturated	Saturated Saturated Unsaturated	Saturated Unsaturated Unsaturated	Unsaturated Unsaturated Unsaturated
Melting point :	45–60° C.	30–45° C.	ca. 0–10° C.	Below 0° C.
Typical examples of individual components:	Palmitostearins Lauromyristins	Oleopalmitostearin Oleodistearin	Palmitodiolein Stearodiolein	Triolein Oleolinoleins

NATURAL FATS :
←——LIQUID FATS——→
←——SOFT SOLID FATS——→
←—HARD SOLID FATS——→

Solid or Semi-Solid Fats (*Crystallised from Acetone at* 0° *to* −10° *or above*) :—
←——Least Soluble——→
←——Intermediate——→
←——Most Soluble——→

Liquid Fats (*Crystallised from Acetone Between* 0° *and* −60°) :—
←—Least Soluble——→
←—Intermediate——→
←——Most Soluble——→

The acetone crystallisation procedure thus divides the natural fat into two, three, or more portions, each of which is investigated as follows :

(*a*) the component acids are determined by ester fractionation ;
(*b*) a portion may be hydrogenated and the tristearin content of the product determined ;
(*c*) where necessary, the fully saturated glyceride content (and its component acids) is determined.

From (*a*) and (*c*), the proportions of mono-unsaturated and of di-unsaturated glycerides (or of di- and tri-unsaturated glycerides) in each portion of the fat follow by simple calculation. If the crystallisation is carried out so that there is reasonable certainty that each resulting portion is either (i) a mixture of fully saturated, mono-unsaturated disaturated, and di-unsaturated monosaturated glycerides or (ii) mixtures containing (*a*) only mono-unsaturated disaturated and di-unsaturated monosaturated glycerides, or (*b*) only di-unsaturated monosaturated with tri-unsaturated glycerides, this is frequently found to give sufficient information to enable the component glycerides to be approximately quantitatively defined.

In some portions of the fat, however, it may be desirable also to determine the total content of tri-C_{18} glycerides in the form of tristearin (as in (*b*) above), and from the tri-C_{18} glyceride content so obtained, coupled with the component acid analyses (*a*), there then follow also the proportions of mono-C_{18} and di-C_{18} mixed glycerides (in which another homologous acid (e.g. palmitic) is present.

In the cases of many solid fats, with these data (and knowing the general order of solubility in acetone of, for example, oleodistearin, dioleostearin, oleopalmitostearin, oleodipalmitin, and palmitodiolein), it is usually possible to give with some confidence a detailed, approximately quantitative statement of the component glycerides in each portion of the fat, and therefrom to deduce that of the original fat.

In the more unsaturated, liquid fats (from which fully saturated glycerides are usually absent) reliance must in general be placed solely on the component acid analyses for each portion obtained by crystallisation, and it is thus the more important in these cases to effect as complete a separation as possible into mixtures of mixed glycerides which include only two of the unsaturated group-types. Here the final quantitative statement of component glycerides may vary from a fairly detailed picture to one in which the fat is described in terms of groups of glycerides, rather than individuals.

The procedure is naturally rather complicated and varies in detail with the nature of the fat under examination; the experimental technique is illustrated further in Chapter XI (pp. 520–526), whilst further details of the technique and of the interpretation of resulting data will be found in communications by Hilditch with Stainsby,[12] Ichaporia,[13] Bushell,[14] Green,[15] Pedelty,[16] Murti,[17] Maddison,[18] S. Paul,[25] Zaky,[26] and by Meara with Atherton,[33] Zaky,[35] and Bjarnason.[37]

Notes on some other applications of the acetone crystallisation procedure to solid and liquid fats.—It seems well to include here a few remarks on applications of the crystallisation procedure, which have recently been published, for purposes other than elucidation of glyceride composition.

The method has been applied [54] to routine technical analysis of hydrogenated fats intended for edible purposes. The part of the fat insoluble in acetone (4 c.c. per gram) at 0° is recrystallised from acetone (10 c.c. per gram) at 15° and then again at 0°; from the proportion of the fractions obtained, and their iodine, thiocyanogen and saponification values, the amount of mono-oleo glycerides and fully saturated glycerides is obtained. Hydrogenation of the crystallised fractions, followed by crystallisation from ether at 27·5° and 21·5°, and determination of their saponification values indicates the proportions of dipalmito- and monopalmito-glycerides present.

Crystallisation of fats from organic solvents has also been proposed for the purposes of (*a*) obtaining more unsaturated oils with improved drying properties from soya bean or similar oils and (*b*) removing the more solid glycerides from oils such as cottonseed or groundnut oils, or their partly hydrogenated products, in order that an oil which will remain completely liquid on standing at moderately cool room temperatures may be produced.

Bull and Wheeler [55a] studied the crystallisation of soya bean oil from a number of solvents at 15° to −76°, and found that acetone, followed by methyl acetate, was the most useful solvent. A high ratio of solvent to oil, together with a very low temperature of crystallisation, was found to give the best results; but it was not possible to obtain, from a soya bean oil of iodine value 132·5, more than 30–60 per cent. yields of most-soluble fractions which had iodine values of only 155–145. With still higher solvent ratio, a low yield of most soluble material was obtained but the iodine value could not be raised above 165. This, of course, is what would be expected, since (as illustrated in Table 65) the tri-unsaturated (and most soluble) glycerides of the oil will be mixed oleo-linoleins, etc. In soya bean oil with not more than 60 per cent. (nearly all linoleic) of unsaturated acids other than oleic acid, the most unsaturated glycerides present, except for small amounts of oleo-linoleo-linolenin (iodine value 174), will therefore be oleodilinoleins (iodine value 144); whereas a linseed oil of iodine value 180, the component acids of which include usually 50 per cent. or more of linolenic and 20–25 per cent. of linoleic, will contain fair proportions of linoleolinolenins, including linoleodilinolenin (iodine value 232) and linolenodilinolein (iodine value 203). Bull and Wheeler, indeed, remark on the fact that, whilst the oil gave the results quoted above on fractional crystallisation, a single crystallisation of the *soya bean oil mixed fatty acids* from acetone at −30° to −50° gives a 50 per cent. yield of most soluble acids of iodine value 180.

Unless, therefore, economic uses for the relatively large proportions of the more saturated fractions of a semi-drying oil are available, the production of fractions with more definitely "drying" values appears doubtful as a commercial proposition. On the other hand, application of fractional crystallisation to a drying oil would obviously improve its value from this point of view.

Kleinsmith and Kraybill [66] have studied the separation of soya bean, cottonseed, linseed, and maize oils by extraction with methyl alcohol at 25° into two liquid phases, with results not very dissimilar from the experience of Bull and Wheeler [55a] with acetone at lower temperatures. A soya bean oil of iodine value 132·5 gave unsaturated fractions of iodine value 140–146.

For a technical object of different character, Bailey *et al.*[67] have crystallised cottonseed and groundnut oils, or their partly hydrogenated forms, from commercial hexane at about −15°, when any disaturated glycerides and some of the monosaturated glycerides in the oils are precipitated, leaving oils which remain clear down to +5° or 0°. Such oils are then suitable for salad oils and other purposes; for instance, a hydrogenated groundnut oil, after separation by this means, furnished a liquid oil of iodine value 76 containing no more linoleic acid than olive oil, and forming a good substitute for the latter either for edible purposes or in textile applications.

These analytical and technical applications of the crystallisation procedure are of sufficient interest to be mentioned here, but their more detailed consideration is beyond the scope of this book.

Attempted separation of glycerides by the "molecular still."—It should also be mentioned here that Riemenschneider *et al.*[68] and Bull and Wheeler [55b] have examined the degree to which mixed glycerides of, respectively, cottonseed and soya bean oils undergo separation when submitted to fractional evaporation in the high vacuum of a "molecular still." Although unsaponifiable matter and free fatty acids were readily separated, the mixed glycerides themselves underwent only slight separation. It does not seem at present that this mode of separation will be able to find much application in the elucidation of glyceride structure in natural fats. (Further references will be found in the work of Embree and other investigators.[70])

Study of solid and semi-solid fats by the acetone crystallisation technique (continued).—Returning to the determination of component glycerides in solid and semi-solid vegetable fats by this method, it may be worth while to illustrate the procedure by details of the results obtained in some of the first instances in which it was employed (cacao butter,[12] mowrah fat,[13] shea butter,[15] phulwara butter,[14a] borneo tallow,[14b] and kepayang (*Hodgsonia*) oil [16]). Table 66 shows the proportions of each fat obtained in different fractions, and the proportions of the component acids in each fraction and in the whole fat. For simplicity of calculation, all data employed in these investigations are referred to a molar (and not weight) percentage basis.

Inspection of Table 66 shows that the glyceride fractions least soluble in acetone contain not more than 40 per cent. of unsaturated acids, and therefore the amount of di-unsaturated-monosaturated glycerides present does not exceed about 20 per cent. and is usually less. In the most soluble fractions, however, the unsaturated acid content ranges from 50 per cent. up to nearly 70 per cent., and it is evident that glycerides containing more than one unsaturated acyl group are concentrated in these portions of the fat.

We will digress here once more to comment on the fact that, in the first five fats in Table 66, the greater part of the linoleic acid is also concentrated in the most soluble portions; in other words, the linoleic acid is present almost wholly in glycerides which also contain an oleic acid group. This feature, at first glance somewhat remarkable, is in reality again merely the natural consequence of the operation of the "rule of even distribution" coupled with the particular fatty acid composition of the five fats in question. In each case, linoleic is a *minor* component acid, whilst oleic and saturated acids (palmitic or stearic, or both) are *major* component acids, each contributing 25 per cent. or more to the total fatty acids. Broadly speaking, the "even distribution" generalisation will therefore have the result that almost all the individual triglyceride molecules will contain at least one acyl group of a major component acid—oleic and saturated; on the contrary, in any triglyceride molecules in which the minor component, linoleic acid, is present, the latter will only be present as a single (monolinoleo-) group. But, since an oleic group is present in nearly every molecule of triglyceride, an oleic group will also be present concurrently in those molecules

TABLE 66. *SEPARATION OF SOLID SEED FATS BY CRYSTALLISATION FROM ACETONE*

	Fractions obtained from Acetone Crystallisation			Whole Fat
	Least Soluble	Intermediate	Most Soluble	
CACAO BUTTER				
Glycerides (mol. per cent.)	26·7	48·8	24·5	100
Component acids (mol. per cent.)				
Palmitic	8·6	32·3	32·9	24·3
Stearic	55·1	31·2	18·5	35·4
Oleic	34·8	36·0	42·5	38·2
Linoleic	1·5	0·5	6·1	2·1
MOWRAH FAT				
Glycerides (mol. per cent.)	21·2	33·3	45·5	100
Component acids (mol. per cent.)				
Palmitic	26·3	24·9	22·5	24·1
Stearic	32·1	20·8	12·1	19·3
Oleic	40·1	39·8	47·7	43·4
Linoleic	1·5	14·5	17·7	13·2
SHEA BUTTER				
Glycerides (mol. per cent.)	49·3	—	50·7	100
Component acids (mol. per cent.)				
Palmitic	5·5		7·1	6·3
Stearic	57·1		23·2	40·0
Oleic	36·5		62·8	49·8
Linoleic	0·9		6·9	3·9
PHULWARA BUTTER				
Glycerides (mol. per cent.)	72·4	—	27·6	100
Component acids (mol. per cent.)				
Palmitic	65·0		44·9	59·4
Stearic	2·3		2·5	2·4
Oleic	31·7		41·6	34·5
Linoleic	1·0		11·0	3·7
BORNEO TALLOW				
Glycerides (mol. per cent.)	54·0	32·5	13·5	100
Component acids (mol. per cent.)				
Palmitic	12·5	30·2	21·8	19·5
Stearic	53·4	31·7	24·1	42·4
Arachidic	1·1	1·0	1·1	1·0
Oleic	33·0	37·1	51·4	36·9
Linoleic	—	—	1·6	0·2
KEPAYANG OIL				
Glycerides (mol. per cent.)	44·2	—	55·8	100
Component acids (mol. per cent.)				
Myristic	0·6		0·6	0·6
Palmitic	44·8		33·0	38·2
Stearic	15·8		3·8	9·0
Arachidic	0·4		0·2	0·3
Hexadecenoic	2·5		3·1	2·9
Oleic	17·2		32·1	25·5
Linoleic	18·7		27·2	23·5

in which there is also a linoleic group. Thus, where linoleic acid is a minor component of the whole fat, it is bound to occur in the di- or tri-unsaturated glyceride portions, as a mixed linoleo-oleoglyceride.

The case of kepayang oil, on the other hand, offers a somewhat unusual instance of a fat with approximately equal contents of oleic and linoleic acids, each of which is here a " major " component. Consequently each plays approximately the same part in the development of the mixed glycerides and, as Table 66 indicates, the ratio of oleic and linoleic acids remains much the same in both the mono-unsaturated and the di-unsaturated glycerides present in the fat. This means, of course, that in the mono-unsaturated group the unsaturated radical may be either oleic or linoleic, whilst in the di-unsaturated group there may be oleo-linoleo-, dioleo-, or dilinoleo-glycerides (probably all three, with the mixed type predominating).

The mode of distribution of linoleic acid in the glycerides of the fats in Table 66 thus affords a further and somewhat striking example of the general operation of the " even distribution " principle.

Let us now return to the further steps necessary to elucidate the glyceride structure of the various portions of the fats in Table 66 as resolved by crystallisation from acetone. As already stated, the proportions of mono- and di-unsaturated, or di- and tri-unsaturated glycerides, present in each portion can be deduced from the component acid analyses after making allowance for any fully saturated glycerides present. Further, determination of the tristearin content of the hydrogenated fractions gives an alternative division of each portion into (i) tri-C_{18} glycerides, (ii) palmitodi-C_{18} glycerides, and (iii) dipalmitomono-C_{18} glycerides. It should be noted here that, of course, the determination of tri-C_{18} glycerides as tristearin prevents any possibility, for the present, of differentiating between oleo- and linoleo-glycerides.

For convenience, the use within inverted commas of the terms " oleo-" or " olein " is intended to denote that the unsaturated group may in fact be either oleic or linoleic.

Full details will be briefly described here with reference to two fats only, cacao butter and shea butter.

Cacao butter. The relevant data are given in Table 67A.

TABLE 67A. *COMPOSITION OF FRACTIONS A, B, AND C OF THE CACAO BUTTER (MOL. PER CENT.)*

Fraction :	A	B	C
Molar proportion of whole fat	26·7	48·8	24·5
(*a*) *Component acids present :*			
Palmitic	2·3	15·8	8·1
Stearic	14·7	15·2	4·5
Oleic (+linoleic)	9·7	17·8	11·9
(*b*) *Component glycerides present :*			
Tri-C_{18} glycerides	19·5	5·9	5·0
Palmito-di-C_{18} glycerides	7·2	38·5	14·9
Dipalmito-mono-C_{18} glycerides	—	4·4	4·6
(*c*) Mono-" oleo "-disaturated glycerides	24·3	44·2	8·3
Di-" oleo "-monosaturated glycerides	2·4	4·6	13·7

(*a*) From component acid analyses (Table 66).

(*b*) From tristearin determined in completely hydrogenated fractions, with (*a*), as above.

(*c*) From proportions of unsaturated and saturated acids in (*a*), triolein being taken as absent and fully saturated components as only in fraction C (*vide infra*).

A fairly close estimate of the individual components of the three fractions can now be reached by taking into account the following considerations :

(*a*) Oleodistearin is the least soluble in acetone of the mixed glycerides present and would be expected to be concentrated in fraction A, with possibly some in B, while C should not contain it.

(*b*) Both classes of palmito-" oleins " are comparatively easily soluble in acetone in the concentrations employed, and, as a matter of fact, the crystallisation data show that A contains no dipalmito-C_{18} glycerides. Fractions B and C, however, contain about equal proportions of them. The location of the fully saturated dipalmitostearin (2·5 per cent. of the whole fat) was felt to be somewhat uncertain in this particular instance, (one of the earliest in which the procedure was used), but was taken as wholly in fraction C. The comparatively soluble palmito-di-" oleins " have apparently also all passed into fraction C. On the other hand, stearodi-" oleins " appear in each fraction, but to a smaller extent in A than in B and C.

The final estimate of the cacao butter glycerides is therefore as given in Table 67B.

TABLE 67B. *ESTIMATED COMPONENT GLYCERIDES OF CACAO BUTTER (MOL. PER CENT.)*

	FRACTION A	FRACTION B	FRACTION C	WHOLE FAT
Fully Saturated (2·5 per cent.)				
Dipalmitostearin	—	—	2·5	2·5
Mono-oleo-glycerides (76·8 per cent.)				
Oleodipalmitins	—	4·4	2·1	6·5
Oleopalmitostearins	7·2	38·5	6·2	51·9
Oleodistearins	17·1	1·3	—	18·4
Dioleo-glycerides (20·7 per cent.)				
Palmitodiolein	—	—	8·7	8·7
Stearodiolein	2·4	4·6	5·0	12·0

Shea butter. The corresponding experimental data for this fat are in Tables 68A and 68B.

TABLE 68A. *COMPOSITION OF FRACTIONS A AND B OF THE SHEA BUTTER (MOL. PER CENT.)*

Fraction :	A	B	TOTAL
Molar proportion of total glycerides	49·3	50·7	100·0
(*a*) *Component acids present :*			
Palmitic	2·7	3·6	6·3
Stearic	28·2	11·8	40·0
Oleic	18·0	31·8	49·8
Linoleic	0·4	3·5	3·9
(*b*) *Component glycerides present :*			
Tri-C_{18} glycerides	44·3	39·9	84·2
Palmitodi-C_{18} glycerides	1·9	10·8	12·7
Dipalmitomono-C_{18} glycerides	3·1	—	3·1
Fully saturated glycerides	4·5	—	4·5
(*c*) Mono-" oleo "-disaturated glycerides	34·4	—	34·4
Di-" oleo "-monosaturated glycerides	10·4	46·2	56·6
Tri-" olein "	—	4·5	4·5

(*a*) From component acid analyses (Table 66).

(*b*) From tristearin determined in completely hydrogenated fractions, with (*a*), as above.

(*c*) From proportions of unsaturated and saturated acids in (*a*) (see also below).

The following reasoning was applied to the above data:

Fraction A. The fully saturated components (palmitostearins) appear in this fraction. From their observed component acids, they consist of about 3 per cent. of dipalmitostearin and 1·5 per cent. of palmitodistearin, and account for nearly all the palmitic acid in this fraction.

The remaining 44·8 per cent. of the total glycerides, represented in fraction A, contains molar proportions of 26·4 per cent. saturated and 18·4 per cent. unsaturated acids. Tri-" olein " will have passed with the acetone-soluble components into fraction B, and the 44·8 per cent. is therefore a mixture of mono-" oleo "-disaturated (34·4 per cent.) and di-" oleo "-monosaturated (10·4 per cent.) glycerides. The small residue of palmitic acid unaccounted for as fully saturated glyceride may be present either as oleopalmitostearin or palmitodiolein; in either case the amount is too small to be assessed by the analytical methods available. In accounting quantitatively for the fatty acid components in Table 68B, this has been arbitrarily credited as palmitodiolein. The greater part of fraction A, however, consists of oleodistearin and stearodiolein.

Fraction B. The amount of tri-" olein " is an uncertain factor here. The molar proportions of the components of fraction B include 15·4 per cent. saturated and 35·3 per cent. unsaturated acyl groups, present either as mixed saturated-unsaturated or wholly unsaturated glycerides. The figures correspond with either a mixture of 46·2 per cent. of monosaturated-di-" oleo "-glycerides with 4·5 per cent. of tri-" oleins " (as in Table 68A), or a mixture of 23·1 per cent. of mono-" oleo "-disaturated glycerides with 27·6 per cent. of tri-" oleins," or any ternary mixture falling within these limits. The possibility of tri-" oleins " approaching the upper limit is ruled out because this would connote a correspondingly high proportion of oleodistearin in fraction B, which is in contradiction to the known sparing solubility of this glyceride in cold acetone. The assumption that fraction B is a mixture of di- and tri-unsaturated glycerides cannot therefore be far from the truth. At the same time, it must be made clear that the figure of 4·5 per cent. for tri-" olein " is a minimum; it may in fact be somewhat (but probably not much) greater, in which case a small proportion of mono-" oleo "-disaturated glycerides—probably " oleo "-palmitostearin—would also be present in this fraction.

Having regard to the above considerations and limitations, it is believed that Table 68B illustrates the most probable composition of the glycerides present in shea butter and that the proportions of the major components, at all events, are indicated therein with a reasonable degree of accuracy.

TABLE 68B. *ESTIMATED COMPONENT GLYCERIDES OF SHEA BUTTER (MOL. PER CENT.)*

	Fraction A	Fraction B	Whole Fat
Fully saturated (4·5 per cent.)			
Dipalmitostearin	3·0	—	3·0
Palmitodistearin	1·5	—	1·5
Mono-" oleo "-glycerides (34·4 per cent.)			
" Oleo "-distearins	34·4	—	34·4
" Oleo "-palmitostearins	*	*	*
Di-" oleo "-glycerides (56·6 per cent.)			
Palmitodi-" oleins "	0·5	10·8	11·3
Stearodi-" oleins "	9·9	35·4	45·3
Tri-" oleins " (4·5 per cent.)	—	4·5†	4·5

* Small proportions of " oleo "-palmitostearins may possibly be present.

† Minimum figure; the actual amount of tri-unsaturated glycerides cannot, however, be greatly in excess of this.

The approximate compositions deduced by this procedure for the fats listed in Table 66 are shown in the next table (69).

TABLE 69. *COMPONENT GLYCERIDES PRESENT IN CERTAIN SOLID SEED FATS*

	Cacao Butter Per Cent. (Mol.)	Mowrah Fat Per Cent. (Mol.)	Shea Butter Per Cent. (Mol.)	Phulwara Butter Per Cent. (Mol.)	Borneo Tallow Per Cent. (Mol.)	Kepayang Oil Per Cent. (Mol.)
Fully saturated glycerides:						
Tripalmitin	—	—	—	8	1	2
Dipalmitostearin	2	1	3	—	2	0·5
Palmitodistearin	—	—	2	—	1	—
Mono-" oleo "-glycerides:						
Oleodipalmitins	6	1	—	62	8	33
Oleopalmitostearins	52	27	Traces	7	31	27
Oleodistearins	19	—	35	—	40	—
Di-" oleo "-glycerides:						
Palmitodiolein	9	41	10	23	3	24
Stearodiolein	12	30	45	—	13	—
Triolein (*or oleolinoleins*)	—	—	5	—	—	13

COMPUTATION OF PROPORTIONS OF CHIEF COMPONENT GLYCERIDES OF A FAT FROM ITS FATTY ACID COMPOSITION

If we consider a fat which, in addition to oleic (with linoleic) acid, contains substantially only one saturated acid (e.g. palmitic acid in phulwara butter, or stearic acid in *Allanblackia Stuhlmannii* or *Garcinia* seed fats), and if in such fats there is known to be no significant amount either of trisaturated or of tri-unsaturated glycerides, it is obvious that such fats must be mainly a mixture of mono-" oleo "-disaturated and di-" oleo "-monosaturated glycerides, and (only one saturated acid being concerned) the proportions of each type can be calculated by simple arithmetic from those of the fatty acids present. The fats in Table 66, however, for the most part contain substantial amounts of each of the saturated acids, palmitic and stearic, as well as oleic (with linoleic) acid. It was noticed that the observed amounts of palmitodi-" olein " and of stearodi-" olein " in cacao butter (and, subsequently, in the other fats) could be approximately obtained by calculation if the unsaturated acid in the whole fat were divided, in arithmetical proportion to the palmitic and stearic acid contents, and then each portion combined with the latter so as to give mixtures of monopalmitodi-" oleins " and dipalmito-" oleins," monostearo-di-" oleins " and distearo-" oleins." Such a calculation, of course, cannot take account of the subsidiary amounts of fully saturated or of tri-unsaturated glycerides which experimental determination may show to be present ; but the results obtained show fairly close agreement for those mixed glycerides which are present in large amounts in the fats.

In the case of cacao butter, for example, the molar proportions of the acids in the whole fat were palmitic 24·3, stearic 35·4, and oleic (with linoleic) 40·3. The increments of " oleic " acid corresponding in these proportions to each saturated acid taken separately are :

" Oleic "	16·4	" Oleic "	23·9
Palmitic	24·3	Stearic	35·4

In combination respectively as mono-" oleo "- and di-" oleo "-palmitins or -stearins, these proportions lead to :

	Per Cent. (Mol.)		Per Cent. (Mol.)
Palmitodi-" olein "	9	Stearodi-" olein "	12
" Oleo "-dipalmitin	32	" Oleo "-distearin	47

The proportions thus derived for the di-"oleo" derivatives are almost exactly those found by analysis; but the experimental data show that the corresponding mono-"oleo" derivatives are not present wholly as such, but appear to a great extent as the trebly mixed glyceride "oleo"-palmitostearin (52 per cent.). In other instances we find that the "oleo"-dipalmitin and "oleo"-distearin obtained by calculation, if rearranged so as to give the maximum possible amount of "oleo"-palmitostearin, yield figures which approximate fairly closely to the experimental data.

When the component glycerides in a reasonably large number of fats had been determined by the more detailed methods outlined on pp. 241–248, Hilditch and Meara [59a] reviewed and extended the application of the computation suggested on the previous page. It at once became evident that the choice of the particular acid to be "proportioned" amongst the rest of the component acids of a fat is strictly limited, if data accordant with the experimental findings are to be obtained. In fact, almost always it has been found necessary to partition *oleic acid* amongst the rest. The only exception to this so far observed is in fats in which some other unsaturated acid predominates in amount over oleic acid (e.g. linoleic acid in cottonseed oil, Table 72B; tetradecenoic acid in kombo fat, Table 73); in such instances it has proved essential to divide such *major component unsaturated acid* amongst the rest. Further, in the only case considered in which both oleic and linoleic acids were present in approximately equal proportions (kepayang oil, Table 72B), it appeared that these determined the proportions of tri-unsaturated glycerides present.

Although the basis of the computations under discussion is completely empirical, and has no bearing on the manner in which glycerides may have been assembled by natural processes, it may be said that, to a certain extent, this necessity for partitioning oleic (or other major unsaturated) acid amongst the other acids points to some special function of the unsaturated acids which conditions the general glyceride structure of natural fats.

Briefly, the methods of calculation which were found by Hilditch and Meara to give results most comparable with the experimentally determined glyceride compositions may be summarised as follows:

(*a*) Arithmetical calculation can be applied at present only to fats which contain not more than three, or sometimes four, major component acids.

(*b*) The oleic acid (or sometimes other major component unsaturated acid) is divided amongst the rest of the mixed acids in proportion to the amounts of the latter, and then combined arithmetically with each (e.g. to give oleodipalmitin and palmitodiolein, oleodistearin and stearodiolein, etc.),* and any mono-oleo-glycerides are then re-combined so as to give maximum "even distribution," as exemplified on p. 249.

(*c* In special cases in which oleic acid greatly predominates over the other acids (none of which exceeds in amount 10 per cent. of the total fatty acids), the calculation in (*b*) above simplifies into taking each minor component combined with two oleic acid groups (e.g. palmitodiolein, etc.).

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* It should be noted that experimental investigation and arithmetical computation alike preclude, as a general rule, consideration of more than three fatty acids at a time. Consequently minor components have to be grouped with the nearest related major component acid. Thus, for the purposes under discussion oleic and linoleic acids are frequently considered together as "oleic," and minor proportions of hexa- and tetra-decenoic acids when present may also be included under "oleic"; whilst, similarly, minor amounts of myristic or lower saturated acids may be included under "palmitic," or minor amounts of arachidic with "stearic," etc.

(*d*) In a few instances (cottonseed oil is an important one) in which a major component saturated acid is accompanied by small proportions (less than 5 per cent. of the total acids) of homologous saturated acids (e.g. palmitic by small amounts of myristic and/or stearic), it has been found best first to allow for these minor components as mixed glycerides with an acid group of each of two major component acids, and subsequently to partition oleic acid (or other major component unsaturated acid) amongst the remaining acids. This applies to cottonseed oil (Table 72B), virola and kombo fats (p. 259, Table 73), but does not seem invariably to give closest accordance.

(*e*) In a few vegetable fats which seem not to follow the " rule of even distribution " so closely as the majority (notably palm oil, *cf.* p. 282, Table 75), a further modification has been observed to bring the computed data into closer accordance with the experimentally determined figures. In these cases it has been found that, approximately, the observed proportions of fully saturated and/or tri-unsaturated glycerides observed in such cases are in the region of half that which would be expected if the saturated or unsaturated acids, respectively, were made up on the principle of " random," instead of " even " or " widest " distribution.

Tables 70, 71, and 72 below illustrate the extent to which the experimental findings are reproducible by calculations from the composition of the mixed fatty acids of a fat on the lines suggested in (*a*) to (*e*) above. It may again be pointed out that the calculations rest on a purely empirical basis, but that it is clear that it is essential to divide up the oleic (or other major unsaturated) acid amongst the remaining acids in order to obtain approximate accordance with the values as determined experimentally. In many instances the accordance between experimental and " computed " figures is remarkably close, in a number of other cases the coincidence is by no means so satisfactory ; but, at least, computations on the lines suggested in (*b*), (*c*) and (*d*) above have so far invariably indicated the chief individual glycerides present in a fat, and also the relative order of their proportions.

It may therefore be claimed that a beginning has been made in a direction of some importance, namely, the prediction of the component glycerides in a natural fat from the composition of its total fatty acids.

In the tables which follow will be found a number of instances which illustrate what has been said in the preceding paragraphs. In these tables the results of several modes of calculation are included, in order to emphasise the necessity for following the rules which have been indicated above. The tables deal in turn with fats containing one, two, and three major component acids.

TABLE 70. *FATS WITH ONLY ONE MAJOR COMPONENT ACID AND SEVERAL MINOR COMPONENT ACIDS*

(A) *Almond* [60] *and olive* [18c] *oils*

	ALMOND OIL	OLIVE OILS	
Component acids		I	II
Myristic	1·2	1·2	2·5
Palmitic	4·5	11·8	16·5
Stearic	—	2·1	1·5
Unsaturated C_{14} and C_{16}	—	2·2	2·8
Oleic	77·0	76·4	66·8
Linoleic	17·3	6·3	9·9

TABLE 70.—*continued.*

Component glycerides	FOUND	" CALC." (a)	" CALC." (b)	FOUND	" CALC." (a)	" CALC." (b)	FOUND	" CALC." (a)	" CALC." (b)
Monosatd.-diolein	17	17	11	45	45	36	57	61	42
Monosatd.-oleo-" linolein "	—	—	6	—	—	9	4	—	20
" Linoleo "-diolein	52	52	46	26	26	17	34	38	18
Triolein	31	31	37	29	29	38	5	1	20

(*a*) All minor components combined as dioleo-glycerides.
(*b*) Saturated acids proportioned between oleic and " linoleic " (i.e. linoleic and unsaturated C_{14} and C_{16}).

(B) *Groundnut oil* [60]

Component acids	
Palmitic	10·1
Stearic	3·6
Arachidic, etc.	5·5
Oleic	58·0
Linoleic	22·8

Component glycerides	FOUND	" CALCULATED " (*a*)	" CALCULATED " (*b*)	" CALCULATED " (*c*)	" CALCULATED " (*d*)
Mono-oleodisaturated	1	—	—	—	—
Monosaturated-diolein	11	58	25	34	24
Monosaturated-oleolinolein	45		33	23	34
Linoleodiolein	24	42	36	40	34
Oleodilinolein	—	—	—	3	—
Triolein	19	—	6	—	8

(*a*) All saturated acids combined as di-unsaturated glycerides.
(*b*) Saturated acids proportioned between oleic and linoleic.
(*c*) Oleic proportioned between saturated and linoleic.
(*d*) Linoleic proportioned between saturated and oleic.

(C) *Neem oil* [17a]

Component acids	
Palmitic	16·3
Stearic	14·5
Arachidic, etc.	1·2
Oleic	60·3
Linoleic	7·7

Component glycerides	FOUND	" CALCULATED " (*a*)	" CALCULATED " (*b*)	" CALCULATED " (*c*)	" CALCULATED " (*d*)
" Oleo "-dipalmitin	2	—	—	—	—
" Oleo "-palmitostearin	12	—	—	15	3
Palmitodi-" olein "	33	49	49	33	46
Stearodi-" olein "	34	47	47	32	44
Tri-unsaturated	19	4	4	20 †	7

† Oleodilinolein 4 per cent., linoleodiolein 16 per cent.
(*a*) Unsaturated acids proportioned between palmitic and stearic.
(*b*) Linoleic acid combined as oleolinoleo-palmitin or oleolinoleo-stearin.
(*c*) Oleic proportioned between palmitic, stearic, and linoleic.
(*d*) Linoleic proportioned between palmitic, stearic, and oleic ; then rest of oleic between palmitic and stearic.

For almond, olive, and groundnut oils the best agreement is obtained when the minor component acids are all combined (method (*c*), p. 250) as di-unsaturated glycerides (e.g. palmitodiolein, etc.). It appears, when one acid forms 60 per cent. or more of the whole, and none of the others exceeds 10 per cent., that within narrow limits the latter occur as mono-acyl glycerides in which the remaining two acyl groups are contributed by the major component acid.

Neem oil is interesting because, although oleic acid comprises 60 per cent. of the total acids, palmitic and stearic acids are both present to the extent of about 15 per cent. There is an appreciable proportion (14 per cent.) of mono-"oleo"-disaturated glycerides, and the assumption that all saturated acids may be present exclusively as monopalmito- or monostearo-di-" oleins " no longer holds good. " Proportioning " of one component acid amongst the rest must therefore be employed. Of the various ways in which this can be done, it is only when the oleic acid is divided arithmetically between the palmitic, stearic, and linoleic acids that a " calculated " composition [(*c*) in Table 70C] in good correspondence with the observed data for neem oil is obtained.

FATS WITH ONLY TWO MAJOR COMPONENT ACIDS

These fall into several categories which require separate mention :

(*a*) In *Allanblackia*, *Garcinia*, and a few other seed fats two component acids (stearic and oleic) together comprise 95 per cent. or more of the total acids, and there are only very small proportions of fully saturated glycerides or of tri-unsaturated glycerides. Almost exact agreement between the determined and " computed " values is therefore self-evident in these instances.

(*b*) Two seed fats of the family Myristicaceæ have been studied in detail [33a] and are interesting because the component acids are unusual, and because oleic acid is a minor component in each case : in virola fat the main acids are myristic and lauric, and in kombo fat, myristic and its mono-ethenoid derivative Δ^9-tetradecenoic acid. Whilst accordance between observed and " computed " proportions is at best only approximate, maximum agreement ensues when the chief unsaturated acid (oleic in virola, and tetradecenoic in kombo fat) is proportioned amongst the rest of the acids, followed by further recombinations of the mixed glycerides which result so as to afford maximum " even distribution." Data for these fats will be found in Table 73, p. 259.

(*c*) Another group is similar to (*a*) in that stearic and oleic acids are usually the two main components, but palmitic and sometimes linoleic acids are present as minor components, but usually in greater proportions than in group (*a*). Here, division of the oleic acid amongst the rest of the acids (method (*b*), p. 250) usually gives figures in fair agreement with the observed values (*cf.* Table 71).

TABLE 71. *FATS WITH ONLY TWO MAJOR COMPONENT ACIDS*

(A) *Shea Butter and* Shorea robusta *Fat*

Component acids	SHEA BUTTER[15]	S. ROBUSTA FAT[16b]
Myristic	0·7	—
Palmitic	5·6	4·6
Stearic	40·0	44·3
Arachidic	—	6·2
Oleic	49·8	42·3
Linoleic	3·9	2·6

	SHEA BUTTER					S. ROBUSTA FAT				
	FOUND	CALCULATED				FOUND	CALCULATED			
Component glycerides		(*a*)	(*b*)	(*c*)	(*d*)		(*a*)	(*b*)	(*c*)	(*d*)
Palmitostearins	4	—	—	2	—	2	—	—	6	—
" Oleo "-palmitostearin	Trace	13	11	17	19	8	11	11	11	14
" Oleo "-distearin	35	30	28	18	20	41–45	39	39	27	33
" Oleo "-stearo-arachidin	—	—	—	—	—	14–10	16	15	15	18
Palmitodi-" olein "	10	6	8	—	—	5	2	3	—	—
Stearodi-" olein "	45	47	53	63	61	25–21	28	28	41	35
Arachidodi-" olein "	—	—	—	—	—	4–8	3	4	—	—
Tri-" olein "	5	4	—	—	—	1	1	—	—	—

(*a*) Oleic proportioned between palmitic, stearic (arachidic), linoleic.
(*b*) Unsaturated acids proportioned between palmitic, stearic (arachidic).
(*c*) Stearic proportioned between palmitic (arachidic), oleic, linoleic.
(*d*) Palmitic, linoleic (arachidic) each as -oleostearins; rest of oleic and stearic as oleodistearin and stearodiolein.

(B) *Baku Fat and Phulwara Butter*

Component acids	BAKU FAT[33b]	PHULWARA BUTTER[14a]
Palmitic	4·6	59·0
Stearic	36·5	3·4
Oleic	58·3	34·0
Linoleic	0·6	3·6

TABLE 71—*continued*

	FOUND	CALCULATED			FOUND	CALCULATED			
Component glycerides		(*a*)	(*b*)	MEAN OF (*a*) AND (*b*)		(*a*)	(*c*)	MEAN OF (*a*) AND (*c*)	(*d*)
Palmitostearins	1	—	—	—	8	—	20	10	6
Oleodipalmitin	—	—	—	—	62	78	40	59	71
Oleopalmitostearin	7–3	5	9	7	7	10	8	9	4
Oleodistearin	27–31	18	34	26	—	—	—	—	—
Palmitodiolein	9–14	9	4	6·5	23	12	30	21	19
Stearodiolein	46–41	68	33	50·5	—	Trace	2	1	—
Triolein	10	—	20	10	—	—	—	—	—

(*a*) Unsaturated acids proportioned between palmitic and stearic.

(*b*) Triolein $\propto$ cube of oleic acid content; rest of unsaturated proportioned between palmitic and stearic.

(*c*) Tripalmitin $\propto$ cube of palmitic acid content; unsaturated acids proportioned between stearic and rest of palmitic.

(*d*) Palmitic proportioned between stearic and " oleic."

Baku fat and phulwara butter (the latter exceptional in its high content of palmitic acid) depart somewhat from the normal type of " even distribution," Baku fat containing about 10 per cent. of triolein and phulwara butter about 8 per cent. of fully saturated components (mainly tripalmitin). Naturally, therefore, partition of the oleic acid between the palmitic and stearic acids (in view of the relative proportions of oleic and saturated acids) fails to show either of these respective simple triglycerides and does not give good agreement for the minor components (respectively, oleodistearin and stearodiolein, and oleodipalmitin and palmitodiolein). It is interesting to find, however, that in both fats, contents of all the component glycerides in good accordance with those observed are obtained by taking the mean of the data for each component as calculated (i) by partition of oleic acid between palmitic and stearic acids [columns (*a*) in Table 71B] and (ii) by assuming " random " distribution of one of the acids [columns (*b*) or (*c*) in Table 71B]. In spite of the fact that the proportion (about 60 per cent.) of the major component acid (oleic in Baku fat, and palmitic in phulwara butter) is of an order which in most seed fats is accompanied by pronounced " even distribution," it seems that in these two somewhat exceptional seed fats the major component has become combined with glycerol according to both modes (" random " and " even " distribution) in about equal proportions.

(*d*) Finally, the important palm oils contain only palmitic and oleic acid as major component acids, and they also exhibit some departure from the general rule of " even distribution." As in the case of Baku and phulwara fats, the nearest accordance to the observed glyceride composition is again obtained if the proportion of simple triglycerides (tripalmitin and triolein) is taken as half of that determined on the basis of " random " distribution (i.e. simple triglyceride content $\propto$ cube of the content of the acid in question) ; the remainder of the component glycerides are computed by dividing the residual oleic acid amongst the residual palmitic and other acids as in method (*b*) on p. 250. Numerical data (corresponding to the tables above) for two palm oils will be found later (Table 75, p. 282).

FATS WITH THREE MAJOR COMPONENT ACIDS

Here again several types may be encountered :

(*a*) In cacao butter, borneo tallow, and mowrah fat (which have been mentioned previously, pp. 245–249), oleic, stearic, and palmitic acid are all major components. As Table 72 (A) shows, computation by proportioning oleic between the other two acids gives excellent accordance for the contents of palmito- and of stearo-dioleins, but when the maximum possible amount of oleopalmitostearin is very high, only about 75 per cent. of the theoretically possible amount is actually found, and oleodipalmitin is present as well as oleodistearin.

TABLE 72. *SEED FATS WITH THREE MAJOR COMPONENT ACIDS*

(A) *Oleic, Palmitic, Stearic*

	CACAO BUTTER [12]	BORNEO TALLOW [14]	MOWRAH FAT [15]
Component acids			
Palmitic	26·2	19·5	24·1
Stearic	34·4	42·4	19·3
Arachidic	—	1·0	—
Oleic	37·3	36·9	43·4
Linoleic	2·1	0·2	13·2

	FOUND	" CALC."	FOUND	" CALC."	FOUND	" CALC."
Component glycerides		(*a*)		(*a*)		(*a*)
Palmitostearins	2	—	5	—	2	—
" Oleo "-dipalmitin	6	—	8	—	—	4
" Oleo "-palmitostearin	52	71	31	55	28	27
" Oleo "-distearin	19	11	40	34	—	—
Palmitodi-" olein "	9	8	3	3	40	38
Stearodi-" olein "	12	10	13	8	30	31
Tri-" olein "	—	—	—	—	—	—

(*a*) Unsaturated acids proportioned between palmitic and stearic.

(B) *Oleic, Linoleic, Palmitic*

	COTTONSEED OIL [16b]	KEPAYANG FAT [16a]
Component acids		
Myristic	2·4	0·6
Palmitic	24·4	38·2
Stearic	1·6	9·3
Oleic*	24·9	28·4
Linoleic	46·7	23·5

* The oleic acid figures include minor amounts of tetra- and hexa-decenoic acids (2·3 per cent. in cottonseed oil and 2·9 per cent. in kepayang fat).

	FOUND	CALCULATED				FOUND	CALCULATED			
Component glycerides		(*a*)	(*b*)	(*c*)	(*d*)		(*b*)	(*c*)	(*d*)	(*e*)
Palmitostearins	—	—	—	—	1	3	—	—	3	5
" Oleo "-dipalmitin	8	7	—	2	19	33	17	16	14	20
" Oleo "-palmitostearin	5	5	4	5	3	27	28	28	25	28
Palmitodiolein	—	—	—	—	—	—	3	—	—	—
Palmito-oleolinolein	41	43	56	53	54	24	52	56	52	33
Palmitodilinolein	18	18	21	22	23		—	—	6	—
Oleodilinolein	28	22	19	18	—	13	—	—	—	5
Linoleodiolein	—	5	—	—	—		—	—	—	9

(*a*) Myristic and stearic as -palmitolinoleins; rest of linoleic proportioned between oleic and rest of palmitic.

(*b*) Linoleic proportioned between palmitic, stearic, and oleic.

(*c*) Oleic proportioned between palmitic, stearic, linoleic.

(*d*) Palmitic proportioned between stearic, oleic, linoleic.

(*e*) Tri-unsaturated glycerides ∝ to cube of unsaturated acid content; rest of oleic proportioned between palmitic, stearic, and rest of linoleic.

Cottonseed oil, of course, contains nearly 50 per cent. of linoleic acid in its mixed acids. The values obtained by partitioning either linoleic or oleic acid between the remaining acids of cottonseed oil [(*b*) and (*c*) in Table 72 (B)] only show an indifferent approach to the observed data, although they both serve to indicate the relative proportions in which the chief mixed glycerides (palmito-oleolinolein, oleodilinolein, and palmitodilinolein) are present in the oil. On the other hand, cottonseed oil contains less than 5 per cent. of each of myristic and stearic acids as minor components and, as in the similar cases of virola and kombo fats (p. 253), the best accordance here seems to be obtained by first combining these small amounts of myristic and stearic acids as -palmitolinoleins (method (*c*), p. 250), and then partitioning the rest of the most abundant unsaturated acid (linoleic) between the oleic and the remaining palmitic acid [(*a*) in Table 72 (B)].

Kepayang fat, although containing little more than 50 per cent. of unsaturated acids, was found to include about 13 per cent. of tri-unsaturated glycerides in its components. It follows from the proportions of its component acids that division of either oleic, linoleic, or palmitic acid amongst the rest of the acids [(*b*), (*c*), (*d*) in Table 72 (B)] fails to indicate any tri-unsaturated glycerides and gives wholly discordant values for palmitodi-unsaturated glycerides. On the other hand, concordant values for the tri-unsaturated glycerides of kepayang fat, and fairly good accordance for the other mixed glycerides present, result from calculating the tri-unsaturated glycerides in proportion to the cube of the content of unsaturated acids (" random " distribution) and then, assuming that the 14 per cent. (calc.) of tri-unsaturated glycerides contain oleic and linoleic acids in the same proportions as those in which they occur in the whole fat, partitioning the residual oleic between palmitic, stearic, and the rest of the linoleic acid [method (*e*), p. 251].

Component Glycerides of Some Individual Vegetable Fats

So far, in this chapter, we have been chiefly concerned to demonstrate the general principle which evidently governs the assembling of fatty acids into triglycerides in seed and fruit-coat fats, namely, that of a marked tendency towards maximum even distribution of the acyl radicals throughout the triglyceride molecules. Emphasis has been laid upon the fundamental similarities in seed and fruit-coat glyceride structure as a whole, rather than upon the specific triglycerides present in any particular case (although these have found incidental reference in some instances in the course of the argument). Some data will now be added with regard to the components of some of the more interesting individual fats which have been studied by the methods described either in the present or in the preceding chapter.

As a matter of convenience, these fats will be considered in roughly decreasing order of their content of saturated acids ; that is to say, in both seed and fruit-coat fats, those of highest melting point will be considered first, and those of most unsaturated character last (*cf.* Table 62, p. 234).

SEED FATS

(*a*) SEED FATS CONTAINING OVER 80 PER CENT. OF SATURATED ACIDS IN THEIR COMPONENT FATTY ACIDS

Seed fats of the Palmæ (Table 62, Nos. 1, 2, 4, 6, 7, 8). The very striking similarity in the component fatty acids of this group, which was pointed out in Chapter IV, Table 59B (p. 202), is accompanied by similar identity in their general glyceride structure, if the six fats (coconut, palm kernel, babassu, gru-gru, Tucuma, and *Manicaria saccifera* kernels) which have been examined from this point of view may be taken as a guide.

We need only consider in detail the three fats, coconut,[2] palm kernel,[2] and babassu.[10] From the quantitative results of the oxidation process, it seems that the content of fully saturated glycerides is in each case of an order which leaves the ratio of saturated to unsaturated acids in the remaining part of the fat at approximately 1·4 : 1. Since there is no evidence of any triolein in either fat, their general composition may be summarised as follows :

	COCONUT FAT [2]	PALM KERNEL FAT [2]	BABASSU FAT [10]
	PER CENT. (WT.)	PER CENT. (WT.)	PER CENT. (WT.)
Fully saturated glycerides	84	63	63
Mono-oleo-disaturated glycerides	12	26	30
Dioleo-monosaturated glycerides	4	11	7

The fully saturated components, which form the greater part of the fats, apparently contain the various acids in much the same proportions in which they occur in the whole fats, as will be seen from the following data :

PERCENTAGE (WT.) OF INDIVIDUAL ACIDS (i) IN THE SATURATED ACIDS OF THE WHOLE FAT AND (ii) IN THE COMPONENT ACIDS OF THE FULLY SATURATED GLYCERIDES OF COCONUT AND PALM KERNEL FATS

	COCONUT (1)		COCONUT (2)		PALM KERNEL		BABASSU	
	WHOLE FAT	FULLY SATURATED PART	WHOLE FAT	FULLY SATURATED PART	WHOLE FAT	FULLY SATURATED PART	WHOLE FAT	FULLY SATURATED PART
	PER CENT.	PER CENT.	PER CENT.	PER CENT.	PER CENT.	PER CENT.	PER CENT.	PER CENT.
Caprylic	9	8	9	9	3	2	6	7
Capric	8	9	8	10	9	8	8	9
Lauric	52	51	50	52	58	60	53	48
Myristic	19	19	20	17	17	20	19	25
Palmitic	10	11	10	10	11	6	10	9
Stearic	2	2	3	2	2	4 (?)	3	1

The similarity in the proportions of saturated acids in the fats as a whole and in their fully saturated components is not by any means a general phenomenon, but appears to be confined to those fats in which unsaturated (oleic) acid is a very minor component, and in which, consequently, the fully saturated glycerides form a very large proportion of the fat. In other groups, in which the fully saturated components only amount to a few per cent. of the whole fat, the major component saturated acid of lowest molecular weight is usually found to be relatively concentrated in the fully saturated glycerides, as will be shown later (p. 273).

The fractional crystallisation of the fully saturated components[2] of coconut and palm kernel fats and of the fats as a whole[19] has uniformly failed to reveal the presence of any simple trilaurin but, on the other hand, has indicated that in both fats dilauromyristins are present in considerable quantity. From the point of view of interpretation of glyceride structure it is unfortunate that there are so many saturated acids other than lauric also present in these fats, thus making any investigation by fractional crystallisation methods exceedingly difficult, and also preventing any simple computation, by the method outlined on pp. 249–255, of the glycerides which might be expected in view of the composition of the fatty acids. It is probably safe to infer, from the complex nature of the fully saturated portions and their considerable content of dilauromyristins, that many mixed glycerides are present and that those acids present in greatest amount (i.e. lauric followed by myristic) are in some degree represented proportionately in each of the numerous mixed triglycerides which are undoubtedly present.

Seed fats of Lauraceæ and Myristicaceæ. The glyceride structures of a few seed fats with very low unsaturated acid contents from these families (*cf.* Chapter IV, Table 59A, p. 200) have been studied in detail.

Puntambekar and Krishna[20] state that the seed fat of *Actinodaphne Hookeri* consists very largely of trilaurin, its component acids being 96 per cent. lauric and 4 per cent. oleic acid. Gunde and Hilditch[21] found that the seed fat of another Lauraceous shrub, *Neolitsea involucrata*, contained 87 per cent. of fully saturated glycerides, trilaurin forming about 66 per cent. of the whole fat; the component acids of the whole fat were found to be *n*-decanoic 3, lauric 86, myristic 4, oleic 4, and linoleic 3 per cent., whilst those of the fully saturated components were *n*-decanoic 5, lauric 90, and myristic 5 per cent. The proportions of the saturated acids in the fully saturated components and in the fat as a whole are thus, as in the Palmæ seed fats, not very different; and in the 13 per cent. of mixed saturated-unsaturated glycerides the "association ratio" of saturated to unsaturated acids is 1·2 : 1. The glycerides of this fat therefore conform closely with the "rule of even distribution." Similarly, Child and Nathanael[61] found the seed fat of *Litsea longifolia* to contain as component acids: lauric 91, palmitic 3, stearic 2, and oleic 4 per cent., with 75–80 per cent. of trilaurin in its component glycerides.

Nutmeg butter, the seed fat of *Myristica fragrans*, was examined by the oxidation method by Collin and Hilditch[22a]; it contained 73 per cent. of fully saturated glycerides, whilst its component acids were lauric 1·5, myristic 76·6, palmitic 10·1, oleic 10·5, and linoleic 1·3 per cent. The percentage proportions of the *saturated* acids in the whole fat were accordingly lauric 1·7, myristic 86·8, and palmitic 11·5 per cent., whilst those in the fully saturated part were lauric 2·2, myristic 91·1, and palmitic 6·7 per cent.—again showing little dissimilarity. Owing to the large proportion of myristic acid in the fully saturated glycerides, it necessarily follows that the simple glyceride trimyristin should be present in quantity. If the two remaining saturated acids were distributed, relatively to myristic in the fully saturated components, in the same way as are the unsaturated to the saturated acids in the whole fat ("association ratio" 1·6 : 1), the proportion of trimyristin in the fully saturated glycerides would be about 77 per cent., corresponding to 55 per cent. of trimyristin in the whole fat. Actually Bömer and Ebach[23] isolated 40 per cent. of trimyristin by crystallisation from a sample of nutmeg butter, a figure which probably accords well with that calculated (since this material frequently contains up to 20 per cent. of non-fatty matter).

Atherton and Meara[33a] studied the component glycerides of virola fat (from *Virola surinamensis*) and of kombo fat (from *Pycnanthus Kombo*). In each fat oleic acid is only a minor component but, whereas virola fat is typical of many other Myristicaceæ fats in containing a very high proportion of myristic acid, kombo fat contains in addition about 20 per cent. of Δ^9-tetradecenoic (myristoleic acid) and in this respect is at present unique (*cf.* Chapter IV, pp. 199, 200). Both fats were examined by the acetone crystallisation procedure and the component glycerides found are given in Table 73; this table also includes the values computed by arithmetical methods from the component acids as described on pp. 249–255. It will be seen that proportioning myristic or other saturated acid amongst the rest of the acids leads to no accordance with the observed component glycerides. Better agreement results by partitioning the major component *unsaturated* acid (oleic in virola fat, and tetradecenoic in kombo fat) amongst the rest of the component acids of each fat (columns (*a*) in Table 73); whilst still closer accordance is reached when, in virola fat, the minor component acids palmitic and oleic are first reckoned as lauro-myristo-glycerides, and when, in kombo fat, the minor component acids are considered as tetradeceno-myristo-glycerides (columns (*b*) in Table 73).

TABLE 73. *COMPONENT GLYCERIDES OF VIROLA AND KOMBO FATS*[33a]

VIROLA FAT

Component acids	
Lauric	17·6
Myristic	72·9
Palmitic	4·4
Oleic	5·1

	FOUND	CALCULATED			
Component glycerides		(*a*)	(*b*)	(*c*)	(*d*)
Dilauromyristin	1	—	—	—	—
Laurodimyristin	31	34	25	53	41
Trimyristin	43	39	47	19	39
Lauromyristopalmitin	10	12	13	—	5
Dimyristopalmitin	—	—	—	13	—
Oleolauromyristin	12	6	15	—	7
Oleodimyristin	3	8	—	15	—
Oleomyristopalmitin	—	1	—	—	8

(*a*) Oleic proportioned between lauric, myristic, and palmitic.
(*b*) Palmitic as lauromyristopalmitin ; oleic as lauromyristo-olein ; rest as laurodimyristin and trimyristin.
(*c*) Myristic proportioned between lauric, palmitic, and oleic.
(*d*) Lauric proportioned between myristic, palmitic, and oleic.

KOMBO FAT

Component acids	
Lauric	8·9
Myristic	63·6
Palmitic	2·0
Tetradecenoic	20·8
Oleic	4·7

	FOUND	CALCULATED			
Component glycerides		(*a*)	(*b*)	(*c*)	(*d*)
Laurodimyristin	17	13	15	—	22
Trimyristin	21	15	22	37	—
Dimyristopalmitin	—	3	—	—	5
Tetradecenolauromyristin	10	14	12	27	5
Tetradecenodimyristin	33	38	31	16	52
Tetradecenomyristopalmitin	3	3	6	6	1
Ditetradecenomyristin	7	—	—	—	1
Tetradeceno-oleomyristin	9	7	14	14	2
Oleodimyristin	—	7	—	—	12

(*a*) Tetradecenoic proportioned between lauric, myristic, palmitic, and oleic.
(*b*) Palmitic and oleic each as -tetradecenomyristins ; rest of tetradecenoic proportioned between lauric and rest of myristic.
(*c*) Lauric, palmitic, and oleic each as -tetradecenomyristins ; rest as tetradccenodimyristin and trimyristin.
(*d*) Myristic proportioned between lauric, palmitic, tetradecenoic, and oleic.

The only two well-marked apparent exceptions which have yet been encountered to the " rule of even distribution " in seed fats also belong to the botanical families now under review, and may be briefly considered at this point.

Myristica malabarica seed fat. The endosperm of *M. malabarica* contains large quantities (nearly 50 per cent.) of resinous, non-fatty matter in addition to glycerides, and it is evident that these, since they must be completely separated from the glycerides, increase the difficulties of investigation to a considerable extent. The investigation of the fats obtained from the seeds by extraction with petrol ether and with carbon tetrachloride[8, 24a] showed that much less resinous material is extracted by means of petrol ether, but the amount of fully saturated glycerides in either case was 16–19 per cent. The component acids of the whole fat are also abnormal for a *Myristica* seed fat, since myristic only forms 32 per cent., whilst in addition there is 17 per cent. of palmitic and 3 per cent. of stearic acid, with 48 per cent. of oleic acid. The great majority of other seed fats of the Myristicaceæ (*cf.* Chapter IV, Table 59A, p. 200) are very rich in saturated acids and thus resemble nutmeg butter rather than the fat of *M. malabarica*; the latter is also exceptional in its abundant content of resinous material, some of which may be actually in combination in the form of mixed glycerides. The fat thus appears to be abnormal in more than one respect.

Laurus nobilis (Lauraceæ) seed fat. This fat [24b] contained 34 per cent. (wt.) or 40·5 per cent. (mol.) of fully saturated glycerides, although its component fatty acids were made up of lauric 43, palmitic 6, oleic 32, and linoleic 19 per cent.; and it therefore had an "association ratio" of only 0·4 equivalents of saturated per equivalent of unsaturated acid in the non-fully saturated glycerides. By hydrogenating the fat and submitting the product to fractional crystallisation from ether, Collin showed that there was extremely little tristearin present, so that the content of fully unsaturated glycerides in the original fat must have been very small. The crystallisation data for the hydrogenated fat thus point unmistakably to a composition approximating to the "even" type, and, if this be the case, it is the lauric acid components in this instance which give rise to the high content of trilaurin. This is also borne out by the fact that, of the lauric acid combined in the whole fat, fully 75 per cent. is present in the fully saturated glycerides, whereas only 25 per cent. of the total palmitic acid is therein represented. If, therefore, the lauric acid be considered separately, the rest of the component acids (oleic, linoleic, palmitic, and a little lauric) are apparently built into glycerides on the usual lines met with in so many other seed fats. Whether the two groups of acids occur, in *Laurus nobilis*, in different parts of the seed, or whether they arrive or develop in the seed at different periods, it is not possible to say at present.

Collin's data (34 per cent. of fully saturated glycerides containing 95 per cent. of lauric acid) suggest the presence of about 31–32 per cent. of trilaurin in the whole fat; Bömer and Ebach [23] actually isolated 30 per cent. of trilaurin by fractional crystallisation of laurel fat.

Dika fats (Simarubaceæ). It will be seen from the table of component acids (Chapter IV, Table 59A, p. 201) that there is more than one variety of dika fats (from species of *Irvingia*). The seed fats of *I. Barteri* (Nigeria) and *I. Olivieri* (cay-cay fat, Cochin China) appear to be closely similar, their component acids including about 40 per cent. of lauric and 55 per cent. of myristic acid. There seem to be two varieties of *I. gabonensis* (Sierra Leone): in one the fatty acids include about 10 per cent. of oleic acid, with 70 per cent. of myristic acid and 20 per cent. of lauric acid, but in the other there is only about 2 per cent. of oleic acid, with nearly 60 per cent. of lauric and about 33 per cent. of myristic acid.

Dika fat from *I. Barteri* was examined by Collin and Hilditch.[22b] Its component acids were lauric 38·8, myristic 50·6, and oleic 10·6 per cent. (wt.), and it contained 79 per cent. of fully saturated glycerides (component acids lauric 43, myristic 57 per cent.). No evidence for the presence of trilaurin or trimyristin in appreciable amounts was forthcoming, and the probable glyceride structure of the fat was considered to be:

	PER CENT.
Dilauromyristins	31
Laurodimyristins	48
Oleo-di-(lauromyrist)-ins	18
Lauro- or myristo-dioleins	3

A dika fat of the almost saturated type from *I. gabonensis* was later investigated by Bushell and Hilditch.[14c] Its component acids were *n*-decanoic

3·1, lauric 58·6, myristic 33·4, palmitic 2·0, stearic 1·1, and oleic 1·8 per cent. (wt.). Systematic crystallisation from acetone yielded a number of fractions, none of which was a completely individual mixed glyceride; but it was clear that the main component was dilauromyristin and that this formed about 65 per cent. (mol.) of the whole fat. Oleo-glycerides were shown to account for 6 per cent. (mol.) of the fat, and to have a composition close to that of oleolauromyristin, the remaining 30 per cent. of the fat probably consisting of about equal proportions of laurodimyristin and *n*-decanolauromyristin with small amounts of palmito- or stearo-lauromyristins.

Both the above dika fats therefore conform closely with the usual rule of " even distribution."

(*b*) SEED FATS CONTAINING 40–65 PER CENT. OF SATURATED ACIDS IN THEIR COMPONENT FATTY ACIDS

This group has received considerable attention in recent investigations for, although only two or three of these fats possess any intrinsic technical importance, they form a particularly interesting section in the following respects:

(i) They include the small number of tropical seed fats in which stearic acid is a prominent component.

(ii) Where the proportion of saturated acids in the whole fat approaches but does not exceed 60–65 per cent., there are just sufficient unsaturated acids to link up in mixed triglycerides with all the saturated acids, 1·3 to 1·5 mols. of saturated acid being therein associated with each mol. of unsaturated (oleic) acid; and in each of these cases the fully saturated glyceride content is very small or almost negligible and supports the general rule. Indeed, the extent to which the generalisation holds over this, the most critical, range of relative proportions of saturated and unsaturated acids is probably the strongest evidence so far put forward of the marked tendency to " even distribution " in seed fats.

(iii) This group of fats is, consequently, rich in mono-unsaturated-disaturated glycerides which, in the course of the oxidation process, yield corresponding monoazelao-disaturated glycerides in quantities sufficient to permit of their isolation and further examination.

(iv) These fats have also provided a certain amount of evidence which suggests that definite forms of specific glycerides, e.g. β-oleodistearin, may be favoured in the natural synthesis of seed fats. This is a most important line of investigation, which will receive much more attention in the near future (*cf.* p. 271), now that thermal and X-ray data for individual members of the mixed triglyceride series are being made available (*cf.* Chapter X, pp. 447–453, Tables 99–104).

(v) Most of these fats contain either palmitic and stearic, or stearic and arachidic, acids as the major component saturated acids, and it is interesting to observe how far the generalisation seems to hold that the acid of lower molecular weight tends to concentrate in the fully saturated glycerides. This is considered on p. 273, after the individual fats have been discussed.

Seed Fats of Sterculiaceæ and Dipterocarpaceæ (in which Palmitic and Stearic are the Major Saturated Component Acids)

Cacao butter (Sterculiaceæ). The extensive use of this fat in chocolates and other confectionery has naturally caused much attention to be paid to its glyceride structure, which has been the object of many investigations. Its special suitability in confectionery lies in the fact that it possesses a comparatively low melting point (about 30°) which is nevertheless much sharper than that of most fats, whilst in the solid state the material is comparatively brittle and not very greasy to the touch. These physical properties are, again, the result of the particular glyceride structure of this fat which, owing to the relative proportions of the few component acids of the fat and its conformity with the general rules of seed fat glyceride structure, is made up for the greater part of mono-oleo-disaturated glycerides, chiefly oleopalmitostearin.

The qualitative crystallisation studies of Klimont (*cf.* Chapter V, p. 225) indicated the absence of simple triglycerides and the presence of oleodistearin and oleopalmitostearin. In 1924 Amberger and Bauch[27] studied, more quantitatively, the fractional crystallisation of cacao butter which had been hydrogenated until its iodine value was reduced to 5·9, and stated that in their opinion the main components were α-palmitodiolein 55, α-oleodistearin 25, and β-palmito-oleostearin 20 per cent. These figures did not tally with the component acid proportions in the whole fat, but Miss E. Lewkowitsch[28] subsequently showed that by adopting a legitimate alternative assumption in the calculations involved, and by taking into account the components in 17·5 per cent. of the fat which was not recovered in Amberger and Bauch's crystallisation, the resulting data (α-palmito-oleostearin 56, β-oleodistearin 26·5, β-palmitodiolein 17·5 per cent.) accorded well with the component acid percentages for the whole fat and also with the work next to be mentioned below. (It is now known,[12] however, that a hydrogenated cacao butter of iodine value 6 still contains about 20 per cent. of oleo-disaturated glycerides which, being relatively soluble, probably account for the " loss " of 17·5 per cent. recorded by Amberger and Bauch.)

In 1927 Hilditch and Lea studied cacao butter by the oxidation method[1, 29] and showed that it contained about 2·5 per cent. of fully saturated glycerides (mainly dipalmitostearins); it is almost certain that the amount of triolein present is negligible, and consequently the remainder of the fat consists of about 73 per cent. of mono-oleo-disaturated glycerides and about 24·5 per cent. of dioleo-monosaturated glycerides.

Lea actually isolated monoazelao-glycerides from the oxidation products of cacao butter corresponding with about 53 per cent. of mono-oleo-disaturated glycerides therein, and obtained a further 15–20 per cent. of monoazelao-glycerides in a less pure condition; so that to this extent the suggested proportion of mono-oleo-disaturated glycerides in the whole fat has been confirmed by chemical analysis. Fractional crystallisation of the monoazelao-glycerides indicated that they contain about 80 per cent. of azelaopalmitostearin, the remainder being mainly azelaodistearin; it was therefore considered probable that about 60 per cent. of the whole fat consisted of oleopalmitostearin.

In 1935 Hilditch and Stainsby[12] separated cacao butter into three fractions by systematic crystallisation from acetone and therefrom deduced the approximate proportions of each of the mixed glycerides present. The details of this work have already received notice earlier in this chapter (pp. 246–248); the final results are quoted again below, together with those of the earlier quantitative attempts to determine the components of this fat:

GLYCERIDE TYPES:	FULLY SATURATED	MONO-OLEO-DISATURATED	DI-OLEO-MONO-SATURATED
Amberger and Bauch (as re-interpreted by Dr. E. Lewkowitsch).	Traces (tristearin and palmitodistearin).	80 per cent. (55 per cent. α-palmito-oleostearin, 25 per cent. oleodistearin).	20 per cent. (β-palmitodiolein).
Lea	2·5 per cent. (palmitostearins).	73 per cent.* (at least 50–60 per cent. oleopalmitostearins).	24·5 per cent.
Hilditch and Stainsby	2 per cent. (palmitostearins).	77 per cent. (52 per cent. oleopalmitostearin, 19 per cent. oleodistearin, 6 per cent. oleodipalmitin).	21 per cent. (9 per cent. palmitodiolein, 12 per cent. stearodiolein).

* Monoazelao-glycerides (i) corresponding with 53 per cent. of mono-oleo-glycerides isolated as pure sodium salts, and (ii) corresponding with about 70 per cent. of mono-oleo-glycerides by separation as lithium salts.

Hilditch and Stainsby were able to isolate, from partially and completely hydrogenated specimens of cacao butter, such large proportions of β-palmitodistearin that it was clear that much, if not all, of the palmitodi-C_{18} glycerides present in the fat possessed this configuration—β-palmito-oleostearin and probably β-palmitodiolein ; on the other hand, β-oleodipalmitin and β-oleodistearin are probably the isomerides of these types mainly present. The assumption of Amberger and Bauch that α-palmito-oleostearin is the form of the trebly mixed glyceride present is inconsistent with the results obtained by Hilditch and Stainsby.

The proportions of stearodioleins and palmitodioleins observed by Hilditch and Stainsby are almost exactly those which would result if the unsaturated acids of the fat were divided in the relative proportions of the palmitic and stearic acids, and united separately with the latter to form mono- and di-oleo-glycerides. Of the total mono-oleo-glycerides, two-thirds are oleopalmitostearins, the remaining third alone consisting of either oleodistearins or oleodipalmitins.

The molar proportions of oleopalmitostearin (52), oleostearins (31), and oleopalmitins (15) are in the order characteristic of even distribution of the total fatty acids (oleic 40, stearic 34, palmitic 26) among the triglyceride molecules, but while the amount of oleodistearins is greater than that of stearodioleins, that of oleodipalmitins is less than that of palmitodioleins. Further, nearly half of the fat is made up of binary combinations in which stearic and oleic, or palmitic and oleic, acids are concerned, but similar combinations with palmitic and stearic acid occur in insignificant quantities.

Borneo tallow (Dipterocarpaceæ). Hilditch and Priestman[30] found that a specimen of this fat (component acids: myristic 1·5, palmitic 21·5, stearic 39·0, oleic 38·0 per cent. wt.) contained 4·5 per cent. of fully saturated palmitostearins, and (no triolein being detected) 17·5 per cent. of dioleo-monosaturated glycerides with 78 per cent. of mono-oleo-disaturated glycerides (the equivalent of 64 per cent. of the latter being definitely isolated in the form of sodium or lithium salts of monoazelao-disaturated glycerides).

Bushell and Hilditch[15] applied the acetone crystallisation procedure to Borneo tallow (component acids: palmitic 18·0, stearic 43·3, arachidic 1·1, oleic 37·4, linoleic 0·2 per cent. wt.) and concluded that the component glycerides were approximately as follows : oleodistearin 40, oleopalmitostearin 31, stearodiolein 13, palmitodiolein 3, oleodipalmitin 8 and fully saturated (mainly palmitostearins with a little tripalmitin and tristearin)

5 per cent. (mol.). The fully saturated glycerides are slightly higher than usual for a fat of this mixture of saturated and unsaturated acids, but otherwise Borneo tallow follows the rule of " even distribution " very closely. With more stearic and less palmitic acid present than in cacao butter, the fat contains more oleodistearin and less oleopalmitostearin than the latter, resulting in a somewhat harder fat of higher " melting point." The proportions of palmito- and stearo-dioleins are calculable within a few units per cent. from the component acids by the arithmetical formula discussed on p. 249, but the amount of oleopalmitostearin, as in cacao butter, falls considerably short of the maximum possible by calculation.

The fat in the nuts of *Shorea robusta* (a tree of north India related botanically to the East Indian *S. stenoptera,* the source of Borneo tallow) was examined by Hilditch and Zaky[26b] by the acetone crystallisation method. With component acids palmitic 4·5, stearic 44·2, arachidic 6·3, oleic 42·2 and linoleic 2·8 per cent. (wt.) the chief component glycerides were " oleo "-distearin 42, stearodi-" olein " 25, " oleo "-arachidostearin 14, " oleo "-palmitostearin 8, with small proportions of arachidodi-" olein " (4) and of tri-unsaturated and fully saturated glycerides (1 per cent. (mol.) each). The proportions of the four main components are closely simulated if the oleic acid is arithmetically proportioned between the various saturated acids as described on p. 250 (*cf.* Table 71, p. 253).

The seed fat of another denizen of Borneo, a member of the Burseraceæ (*Dacryodes rostrata*), was studied by Hilditch and Stainsby[31] (the results were published erroneously as referring to the seed fat of *Sterculia fœtida*). The fat had as component acids: palmitic 11·7, stearic 39·8, arachidic 1·9, oleic 43·3, and linoleic 3·3 per cent. (mol.) and contained less than 2 per cent. of fully saturated glycerides. The main components are probably mono-oleo-disaturated glycerides about 57, and stearo- or palmito-dioleins 41 per cent. ; monoazelao-disaturated glycerides were isolated in the form of sodium salts from the oxidised glycerides in amount corresponding to 43 per cent. of mono-oleo-disaturated glycerides in the original fat.

Seed Fats of Guttiferæ and Sapotaceæ (in which Stearic Acid is frequently the Most Prominent Saturated Acid, whilst Palmitic Acid is also present)

Allanblackia fats (Guttiferæ). These are of little technical importance, but have been exceptionally useful in the study of glyceride structure, because they are built up almost wholly from stearic and oleic acids. It will be recalled that it was in the seed fat of *A. Stuhlmannii* that Heise first demonstrated in 1897 the presence of oleodistearin in quantity in a natural fat; moreover, it has later been possible to isolate this main component almost quantitatively in the pure condition, and to show that it is entirely β-oleodistearin.

A. Stuhlmannii seed fat (component acids: palmitic 3, stearic 52, oleic 45 per cent.) has been studied quantitatively by Hilditch and Saletore,[32] who found it contained only 1·5 per cent. of fully saturated components, and that it could be separated by crystallisation from acetone into nearly 70 per cent. of a solid glyceride (m.p. 42·5–44°, iod. val. 28·5) and a soluble liquid portion of iodine value 56·7 from which no fraction of higher iodine value could be obtained by further crystallisation. The main components are therefore about 66 per cent. of mono-oleo-glycerides (chiefly oleodistearin) and about 33 per cent. of stearo- (with perhaps a little palmito-) diolein. The melting point of the main component is that of β-oleodistearin, and that of the azelaodistearin obtained during oxidation of the fat (63–64°) was unchanged on admixture with β-azelaodistearin prepared by oxidation of synthesised β-oleodistearin.

The seed fats of *A. floribunda* and *A. parviflora* have component acids, and also component glycerides, very closely similar to those of *A. Stuhlmannii*. The molar percentages of component acids and component glycerides observed[35] in these two fats were as follows :

COMPONENT ACIDS.

A. floribunda.	Palmitic 2, stearic 58, oleic 39, linoleic 1.
A. parviflora.	,, 3, ,, 53, ,, 44.

COMPONENT GLYCERIDES

A. floribunda.	Oleodistearin 76, stearodiolein 16, oleopalmitostearin 5, palmitostearins 2, palmitodiolein 1.
A. parviflora.	Oleodistearin 60, stearodiolein 29, oleopalmitostearin 6, palmitostearins 2, palmitodiolein 3.

Garcinia fats (Guttiferæ). These seed fats are also exceptionally rich in stearic acid. The seed fat of *G. morella*, studied by Dhingra, Seth, and Speers,[34] had as component acids: myristic 0·3, palmitic 7·2, stearic 42·5, arachidic 0·3, oleic 43·6, and linoleic 6·1 per cent. (wt.), and contained 2·7 per cent. of fully saturated palmitostearins ; the main portion of the glycerides consists of about 45 per cent. of oleo-disaturated glycerides and nearly 50 per cent. of dioleo-monosaturated glycerides. Another specimen of this fat was examined by Hilditch and Murti[17d] and contained as component acids palmitic 1·2, stearic 48·2, oleic 49·7, linoleic 0·9 per cent. (wt.), with 2 per cent. fully saturated glycerides (tristearin), about 46 per cent. of oleodistearin and about 48 per cent. of stearodiolein.

The seed fat (kokum butter) of *G. indica* was found by the latter workers[17d] to contain as component acids: palmitic 2·5, stearic 56·4, oleic 39·4, and linoleic 1·7 per cent. (wt.); it had 1·5 per cent. of fully saturated glycerides and was composed mainly of about 68 per cent. of oleodistearin and about 20 per cent. of stearodiolein, with 8 per cent. of oleopalmitostearin. Somewhat earlier a specimen of kokum butter had also been submitted to the crystallisation procedure by Vidyarthi and Rao,[62a] who found it to contain as component acids: myristic 1·2, palmitic 5·3, stearic 52·0, and oleic 41·5 per cent., with 59 per cent. of oleodistearin, 21 per cent. of stearodiolein and 14 per cent. of oleopalmitostearin as its chief component glycerides.

Vateria indica seed fat (Dipterocarpaceæ). This seed fat, known technically as Malabar tallow or Dhupa tallow, has been examined by Venkatarao and Narasingarao,[63] who gave its component acids as myristic 0·7, palmitic 13·0, stearic 43·1, arachidic 0·4, oleic 42·5, and linoleic 0·1 per cent., and found that its chief component glycerides included oleodistearin 45, oleopalmitostearin 17, stearodiolein 16, palmitodiolein 13, and oleodipalmitin 7 per cent.

Njatuo tallow, Taban merah fat (Palaquium oblongifolium, Sapotaceæ). This fat was found by Hilditch and Stainsby[31] to possess component acids : myristic 0·2, palmitic 5·9, stearic 54·0, oleic 39·9 per cent. (wt.), and to contain only 1·8 per cent. of fully saturated glycerides. Crystallisation from acetone yielded nearly 50 per cent. of a crystalline solid, m.p. 42·5–44°, evidently β-oleodistearin, whilst the most soluble fractions did not exceed in iodine value that of stearodiolein (57·3). Triolein is therefore not present, and the chief component of the fat is about 77 per cent. of oleo-disaturated glycerides (mainly β-oleodistearin), whilst about 21 per cent. of stearo- (with a little palmito-) diolein is also present. (Calculation from the molar percentages of the component acids (*cf.* p. 249) suggests the possible presence of oleodistearin 63, oleopalmitostearin 18, stearodiolein 17, and palmitodiolein 2 per cent.)

Kanya butter (Pentadesma butyracea, Guttiferæ). Hilditch and Saletore[32] give the probable composition of this fat (component acids: palmitic 5·4, stearic 46·1, oleic 48·5 per cent. wt.) as 3 per cent. of fully saturated palmitodistearins and about equal proportions (47–50 per cent.) of oleo-disaturated and dioleo-monosaturated glycerides. The monoazelaoglycerides obtained on oxidation of the fat consisted largely of monoazelaodistearin, m.p. 61°, connoting the presence of β-oleodistearin in the fat.

Shea butter (Butyrospermum Parkii, Sapotaceæ). This somewhat important seed fat has also been fully examined by the modern methods. Hilditch and Saletore[32] found that a specimen (component acids: palmitic 8·5, stearic 35·9, oleic 49·9, linoleic 5·3 per cent. wt.) only contained 2·3 per cent. of fully saturated glycerides and, assuming that triolein was present only in negligible proportions, concluded that it contained about 30 per cent. of oleo-disaturated glycerides and about 65 per cent. of dioleo-monosaturated glycerides.* Green and Hilditch,[15] after applying the acetone crystallisation method to another specimen of the fat (component acids: palmitic 5·7, stearic 40·4, oleic 50·0, linoleic 3·9 per cent. wt.), gave the probable approximate composition as stearodi-" oleins " 45, oleodistearin 35, and palmitodi-" oleins " 10 per cent., with minor amounts of palmitostearins (4·5 per cent.), tri-" olein " (4·5 per cent.) and possibly oleopalmitostearin. Apart from slightly higher proportions than usual of trisaturated and triunsaturated components, the fat conformed to the usual " evenly distributed " type.

Madhuca (Bassia) seed fats (Sapotaceæ). Mowrah fat, Illipé butter or mee oil, and phulwara butter are seed fats of this genus grown in India and the East Indies, and have been usually known to the technologist as " *Bassia* seed fats " (*vide* Chapter IV, p. 197). The components of mowrah fat and phulwara butter have been determined by the modern methods, employing preliminary partial resolution by crystallisation from acetone.

Mowrah fat (from *M. latifolia*; component acids: palmitic 22·4, stearic 19·9, oleic 44·3, linoleic 13·4 per cent. wt.) was found by Hilditch and Ichaporia[13] to contain 1·2 per cent. of fully saturated dipalmitostearin. The main components are palmitodi-" oleins " 41, stearodi-" oleins " 30, and " oleo "-palmitostearins 27 per cent.; there may also be about 1 per cent. of " oleo "-dipalmitins or similar small quantities of " oleo "-distearin and of tri-unsaturated glycerides (oleolinoleins). The composition follows closely the prevailing rule in seed fats, and is also simulated by the calculation from the component acid percentages described on p. 249.

* A similar study of shea butter by Bougault and Schuster (*Compt. rend.*, 1931, 193, 362) unfortunately led these authors to deduce a composition for its mixed glycerides which is quite incompatible with the amounts and kinds of the component acids of the fat.

Phulwara butter (from *M. butyracea*; component acids: palmitic 56·6, stearic 3·6, oleic 36·0, linoleic 3·8 per cent. wt.) is remarkable, amongst the other *Madhuca* seed fats or, indeed, those of the Sapotaceæ at large, in that stearic acid is a very minor component and that the only major component acids are oleic and palmitic, the latter in unusually large proportions (the highest yet recorded for any seed fat). Bushell and Hilditch[14a] showed the chief glycerides present to be "oleo"-dipalmitins 62, and palmitodi-"oleins" 23 per cent. The fully saturated components (8 per cent., substantially tripalmitin) are more abundant than is usual in a seed fat with the observed proportions of saturated and unsaturated acids. "Oleo"- palmitostearins may amount to about 7 per cent. of the fat. This fat is thus somewhat out of the common in several respects, but it may be added that triolein is not present in detectable quantities. By crystallisation from acetone, 72 per cent. of the fat was obtained as a crystalline solid which contained (calculated to the original fat) 58 per cent. of oleodipalmitin admixed with 8 per cent. of tripalmitin and 6 per cent. of palmitodi-" oleins"; it may thus prove to be a convenient source for the preparation of a natural oleodipalmitin.

The simple arithmetical proportioning of oleic acid between the rest of the acids fails to give a good reproduction of the observed proportions of the chief component glycerides in phulwara butter; but if it be assumed in this instance that tripalmitin has been produced to the extent of half the quantity demanded by the principle of "*random* distribution," the oleic acid being then distributed amongst stearic, linoleic, and the rest of the palmitic acid in the usual way, the component glyceride figures thus "computed" accord fairly well with those observed experimentally.

Piqui-a kernel fat (Caryocar villosum). This fat, from a member of the family Caryocaraceæ, may be mentioned here because, like that of *Madhuca butyracea*, it is unusually rich in palmitic acid, its component acids being myristic 1·4, palmitic 48·4, stearic 0·9, oleic 46·0, and linoleic 3·3 per cent. (wt.). According to Hilditch and Rigg,[36] it contains 2·5 per cent. of fully saturated glycerides (tripalmitin), and the fat is almost certainly chiefly made up of about 50 per cent. of oleodipalmitin with about 40 per cent. of palmitodiolein (leaving out of account small amounts of minor components).

Seed fats of the Sapindaceæ. Two of these (from Malayan species of the genus *Nephelium*) were studied by Hilditch and Stainsby[31]; they are of special interest because, in contrast to those with which we have just dealt, they contain two major component saturated acids which are in this case stearic and arachidic, instead of palmitic and stearic.

Pulasan fat (from *Nephelium mutabile*; component acids: palmitic 3·0, stearic 31·0, arachidic 22·3, oleic 43·7 per cent. wt.) contains about 63 per cent. of oleo-disaturated glycerides (including apparently both oleostearoarachidin and oleodistearin) and about 35 per cent. of dioleo-saturated glycerides, with only 1·5 per cent. of fully saturated glycerides and no detectable triolein. Direct crystallisation of the fat from acetone yielded 48 per cent. of a solid (iodine value 29·0, equivalent 300·5) which was evidently a mixture of oleostearoarachidin and oleodistearin. The composition of the mixed glycerides suggested by the calculation from component acid percentages (described on p. 249) would be stearodiolein 21, arachidodiolein 13, oleostearoarachidin 49, and oleodistearin 17 per cent.

Rambutan tallow (from *N. lappaceum*; component acids: palmitic 2·0, stearic 13·8, arachidic 34·7, oleic 45·3, eicosenoic (?) 4·2 per cent. wt.)

contains about 43 per cent. of oleo-disaturated glycerides (probably oleostearoarachidin with some oleodiarachidin) and about 55 per cent. of dioleo-saturated glycerides (stearo- or arachido-diolein and probably some oleoeicoseno-saturated glycerides). Only 1·4 per cent. of fully saturated glycerides are present, and triolein is absent.

The purest azelao-disaturated glycerides isolated by crystallisation from the oxidation products of the fat had an equivalent of 835·0 and melted at 65·5° (azelaostearoarachidin 822, azelaodiarachidin 850); direct crystallisation of the fat from acetone yielded 25 per cent. of a solid (m.p. 46°, iod. val. 27·4, equivalent 309·4) which evidently contained both oleodiarachidin and oleostearoarachidin.

The " calculated " composition from the component acid percentages (*cf.* p. 249) suggests the following likely composition for the mixed glycerides: stearodi-" olein " 18, arachidodi-" olein " 35, oleostearoarachidin 32, oleodiarachidin 15 per cent.

Other seed fats in this group. Some more seed fats in this category have been studied, with results which are of specific interest as regards the general problem of glyceride structure.

Neem oil (from *Azadirachta indica*, Meliaceæ; component acids: palmitic 14·9, stearic 14·4, arachidic 1·3, oleic 61·9, linoleic 7·5 per cent. wt.) is a case of a fat in which, whilst palmitic and stearic acids are present in about equal amounts, the total saturated acids form somewhat less than a third of the total fatty acids. It has been examined by Hilditch and Murti[17a] by the acetone-crystallisation procedure and found to contain, approximately, the following glycerides: stearodi-" olein " 34, palmitodi-" olein " 33, tri-" olein " 19, " oleo "-palmitostearin 12 per cent., with about 1·5 per cent. of " oleo "-dipalmitin and about 0·5 per cent. of palmitodistearin. Di-" oleo " glycerides thus form about two-thirds of the fat, although the composition of the mixed acids would permit their maximum amount to reach about 90 per cent. of the whole fat. There is, however, nearly 20 per cent. of tri-unsaturated C_{18} glycerides present, these being quite probably linoleodioleins for the most part, and representing mixed glycerides produced from the two unsaturated acids alone. (*Cf.* p. 252 for data " computed " from the fatty acid composition.)

Sapota oil (from *Acharas sapota*, Sapotaceæ; component acids: lauric 1·6, myristic 6·2, palmitic 12·6, stearic 12·0, oleic 66·2, linoleic 1·4 per cent. wt.), examined by Vidyarthi and Mallya,[62b] resembles neem oil somewhat in its general fatty acid composition. Resolution by crystallisation from acetone, coupled with determination of fully saturated glycerides, indicated that the component glycerides were mainly palmitodiolein 36, stearodiolein 28, myristodiolein 23 per cent. (mol.), with minor amounts of the following: tri-" olein " 5, oleopalmitostearin 5, and mono-oleo-glycerides with two of the lower saturated acyl groups 3 per cent. (mol.). The amount of tri-" olein " again suggests that this is linoleodiolein, and di-" oleo "-glycerides form nearly 90 per cent. of the whole fat (the maximum possible amount of these, from the composition of the fatty acids, would have been 97 per cent., with 3 per cent. of mono-" oleo "-disaturated glycerides and no tri-unsaturated or fully saturated glycerides). Calculating from the component acids by proportioning oleic acid amongst the saturated acids (as on p. 249), the " computed " proportions of component glycerides would be expected to be palmitodiolein 38, stearodiolein 32, myristodiolein 26, mono-oleo-disaturated 4, and triolein *nil* per cent.—the values for the main components being thus (as in other cases) in approximate accordance with the proportions found by experiment.

The seed fat of *Hodgsonia capniocarpa* (Cucurbitaceæ) is interesting because it contains about equal proportions of saturated and unsaturated acids, whilst the latter in turn consist of nearly equal amounts of oleic and linoleic acids. As already pointed out on p. 245, this has the consequence that the mono-unsaturated as well as the di-unsaturated glycerides are found to contain both oleic and linoleic acids in corresponding proportions, whereas when linoleic is a minor, and oleic a major, component acid, the former is almost wholly present in the di-unsaturated glycerides alone. A further consequence is shown in the component glycerides present, as determined by Hilditch, Meara, and Pedelty [16a] by study of the fractions obtained by crystallisation of the fat from acetone: "oleo"-dipalmitins 33, "oleo"-palmitostearins 27, palmitodi-"oleins" 24, and tri-"oleins" 13 per cent. The fat thus differs from others of similar general fatty acid composition (in which linoleic acid is a minor component) in its content of tri-unsaturated glycerides. These are almost certainly mixed oleo-linoleins, and the specific mixture of glycerides encountered in this fat is the consequence of the combination of *four* major component acids (palmitic, stearic, oleic, and linoleic) into mixed triglycerides, whereas in other cases only the *three* acids, palmitic, stearic, and oleic, have been major components. Correspondingly, the simple "calculation" based upon distribution of the one unsaturated acid (oleic) between two saturated acids fails in this case to reproduce the observed composition of the fat; but (*cf.* p. 256) better accordance results, in this instance, by calculating the tri-unsaturated glycerides in proportion to the cube of the content of the unsaturated acids (14 per cent. "random" distribution) and then partitioning the residual oleic acid between palmitic, stearic, and the rest of the linoleic acid.

Baku (*Njave, Dumori*) *fat* (from *Mimusops* (*Dumori*) *Heckelii* (*Njave*), Sapotaceæ; component acids: palmitic 4·4, stearic 35·7, arachidic 1·1, hexadecenoic 0·3, oleic 58·0, linoleic 0·5 per cent. wt.) was studied by Atherton and Meara [33b] by the acetone crystallisation method. This is another instance in which the principle of "even distribution" is not completely followed so far as the unsaturated acids are concerned, for the fat was found to contain 10–12 per cent. (mol.) of triolein, the chief components however being stearodiolein 41–46 per cent. and oleodistearin 27–31 per cent., with subordinate amounts of palmitodiolein (9–14 per cent.) and oleopalmitostearin (3–7 per cent.) and traces (1 per cent.) of palmitostearins. In this case (*cf.* p. 254) the observed proportions of the chief components are approximately reproduced by assuming that triolein has been produced to the extent of half the quantity demanded by the principle of "random distribution," and the rest of the oleic acid built up on the usual lines of partition of the latter amongst the saturated acids of the fat.

The fatty oil from another species of *Mimusops*, the Indian *M. elangi*, contains 64 per cent. of oleic, and 14·5 per cent. of linoleic acid, with about 10 per cent. each of palmitic and stearic in its component acids. This fat also appears to diverge somewhat in its glyceride structure from the normal, for Kartha and Menon,[72] using the acetone-crystallisation procedure, found that 4 per cent. of fully saturated and 14 per cent. of mono-unsaturated disaturated glycerides were present, in spite of the high content of unsaturated acid in the whole fat.

Niam fat (from *Lophira alata*, Ochnacaceæ ; component acids : myristic 1·9, palmitic 27·1, behenic 14·2, lignoceric 2·3, tetra- and hexa-decenoic 1·5, oleic 14·5, linoleic 33·3, docosenoic 5·2 per cent. wt.) is an interesting fat studied by Hilditch and Meara.[59b] It is peculiar (*a*) in containing major proportions of behenic acid in its saturated acids and minor proportions of a docosenoic acid in its unsaturated acids, and (*b*) in containing more than twice as much linoleic as oleic acid—an unusual feature in a seed fat in which approximately one-half of the component acids belong to the saturated series. The fat was resolved into three fractions by crystallisation from acetone at 0° and at 20°, and the general nature of the component glycerides present in each was elucidated. The acidic components being somewhat more complex than usual, it was necessary to assume arbitrarily that the docosenoic acid present was in combination with the two most abundant acids as palmito-linoleo-docosenoin (13 per cent. mol.). The rest of the fat was then found to be made up of monosaturated-oleo-linoleins 40, linoleo-disaturated glycerides 29, monosaturated-dilinoleins 9, and oleo-disaturated glycerides 8 per cent. (mol.) No tri-unsaturated glycerides were observed in this fat.

The individual distribution of the major component saturated acids palmitic and behenic could not be followed very far, but it was observed that each was present in quantity in each of the fractions into which the fat had been separated by crystallisation. It therefore appears that the behenic acid behaves in the same way as the palmitic and stearic acids more commonly present in other seed fats which have been investigated. The *Lophira* fat thus forms a very interesting example of the manner in which glyceride structure seems to be largely independent of the particular component acids which may be present.

The presence of four major component acids in this seed fat makes it difficult to apply the arithmetical computation employed in other cases ; but the relative proportions of monosaturated and disaturated glycerides observed suggest that the usual principles of " even distribution " are followed fairly closely in this instance.

The seed fat of *Buchanania latifolia* (Anacardiaceæ) has been found by Godbole, Gunde and Srivastava [64] to contain, as component acids, palmitic 28·9, stearic 8·1, oleic 57·4, and linoleic 5·5 per cent. (wt.). With a fully saturated glyceride content of only 4·8 per cent. mol. (ca. 2 per cent. tripalmitin and 3 per cent. dipalmitostearin), it is probable that the fat consists mainly of monosaturated di-" oleins," but the more detailed crystallisation procedure was not applied in this instance.

Mango fat (from the kernels of *Mangifera indica*, Anacardiaceæ ; component acids : myristic 0·7, palmitic 8·8, stearic 34·0, arachidic 6·7, oleic 49·8 per cent. wt.), has been separated into fractions from acetone by Pathak, Gunde and Godbole,[73] who deduced the presence of 14 per cent. fully saturated glycerides (9 per cent. palmitodistearin and 5 per cent. tristearin), with 54 per cent. stearodiolein, 16 per cent. oleopalmitostearin, 8 per cent. oleodistearin, and 7 per cent. palmitodiolein. The proportion of fully saturated components is considerably higher than usual for a fat in which saturated acids only form half of the components, and the presence of 1 per cent. of triolein was also reported.

Some general points raised by the study of the more saturated seed fats. We may pause at this point to consider some general features revealed in the course of the examination of this group of fats, in which, owing to the ratio of saturated to unsaturated acids being in the region of 1–1·5 to 1, the operation of " even distribution " is extremely well marked and also, frequently, the fats contain unusually large proportions of one or other individual mixed triglyceride. These features are (i) the apparent occurrence of a selected glyceride configuration amongst components of quite a number of the fats which have been investigated, (ii) the possibility that some natural mixed glycerides should possess optical activity, and (iii) certain regularities in the component acids of the small proportions of fully saturated glycerides which occur in the fats of this group.

Configuration of natural mixed triglycerides. It is still slightly premature to go into this subject in any detail, for it will be found that within the next few years more definite progress will be made in this interesting field than has hitherto been possible. The physical properties of individual mixed triglycerides of definite configuration have hitherto been somewhat uncertain, but progress is becoming more rapid in this direction, especially as regards data on melting and transition points, and on X-ray spectra. Moreover, although it still remains exceptional for an individual constituent of a fat to be isolable by crystallisation processes, the wider range of fats studied enables fats of suitably simple composition to be more freely selected for investigations of this kind, whilst conversion of mixed oleo-glycerides into the corresponding stearo-glycerides by catalytic hydrogenation is also becoming a useful aid to research on the configuration of mixed saturated-unsaturated glycerides.

In the meantime, it is desirable to give a brief summary of the present position, which distinctly suggests the possibility that mixed glycerides, such as, for instance, oleodistearin or palmitodiolein, may only occur in natural fats in one particular configuration.

The most clear-cut case in the seed fats so far is oleodistearin. As mentioned on p. 265, it seemed almost certain that this glyceride, as it occurs to the extent of about two-thirds of the seed fat of *Allanblackia Stuhlmannii*, is entirely β-oleo-$\alpha\alpha'$-distearin, m.p. 42·5–44°. It was also suggestive that the same (β-) oleodistearin had been isolated from kokum butter,[38] cacao butter,[39] Borneo tallow,[40] Njatuo tallow,[31] and *Garcinia* seed fats.[17d] A comprehensive survey of the melting and transition points of the oleodistearin present in each of these fats has since been made by Meara,[65a] as a result of which it is now established conclusively that in all five seed fats it is the symmetrical or β-oleodistearin which is present.

The β-palmitodistearin obtained by Hilditch and Stainsby [12] by hydrogenation of the oleopalmitostearin concentrates from cacao butter indicated that the latter glyceride is largely, if not wholly, β-palmito-oleostearin. Again, there were indications that palmitodiolein, a very common constituent in many fats, also had the symmetrical configuration of β-palmitodiolein, for β-palmitodistearin, which melts at 68°, had been identified in each instance in which palmitodiolein concentrates from a fat were hydrogenated, the isomeric α-palmitodistearin of melting point 65° not being observed. This seemed to apply to the palmitodioleins of olive and cottonseed oils, and also to that in pig depot fat, to be considered in Chapter VII (p. 315). Later, examination by Meara [65b] of the hydrogenated products from oleopalmitostearin concentrates of cacao butter, and of palmitodiolein concentrates from cottonseed oil and from pig back fats, showed that in all these instances the palmitodistearin produced by their hydrogenation had melting and transition points identical with those of the symmetrical or β-palmitodistearin.

Banks, Dean, and Hilditch [41] believe that, although both forms of the respective mixed glycerides may be present, β-palmitodiolein and β-oleodipalmitin predominate in palm oil (*cf.* p. 281). On the other hand, Hilditch and Paul [42] conclude that both α- and β-oleo-(linoleo-) dierucins and α- and β-erucodi-oleins or -linoleins are present in rape oil.

The matter is one of distinct interest, and may in due season prove of some importance in considering the biosynthesis of natural fats in plant or animal. The present evidence is however insufficient to permit more than a brief statement of the facts as they appear at the moment, and further data, based upon improvements in the separation by crystallisation of individual mixed glycerides, and upon the full data now becoming available for the melting and transition points of the latter, must be awaited.

Optical rotatory power in natural fats. When natural organic compounds possess molecular asymmetry, they most frequently, as is well known, occur in one of the optically active, enantiomorphic forms, the presence of an inactive or racemic mixture of enantiomorphs being quite unusual. It is only necessary to mention naturally occurring sugars, terpenes or alkaloids as examples. The most abundant naturally occurring derivatives of glycerol, the fats or triglycerides, have never been found to possess optical rotatory power, although other natural glycerol derivatives, such as the α-glyceryl higher acyl ethers (e.g. batyl alcohol) possess small but definite rotatory powers. Again, natural α-glycerophosphoric acid, closely related to the phosphatides and phosphatidic acids, is optically active.

Of course, in symmetrical triglycerides of the type of β-oleodistearin or β-palmitodistearin, mentioned in the preceding section, in which two identical acyl groups are attached to the terminal (α-) hydroxyl groups of the glycerol molecule and a different acyl group to the central (β-) hydroxyl group, no molecular asymmetry and therefore no optical activity is present. On the other hand, when the central (β-) carbon atom of the glycerol carbon-chain is united with four *different* groups, it becomes asymmetric and there is a possibility of optical activity. This happens in the case of an unsymmetrically arranged triglyceride which contains only two fatty acids (e.g. α-oleodistearin or α-palmitodistearin), and also in the case of triglycerides (very many of which occur in nature) in which three different fatty acids are present in the same molecule.

The synthetical work of H. O. L. Fischer and E. Baer [67] has, in fact, opened up the possibility that such natural triglycerides may after all be confined to one enantiomorphic form, and not be racemic compounds. These investigators showed that, whilst synthetic mono- or di-glycerides of higher fatty acids had a slight but definite rotatory power ($[\alpha]_D$ −2° to −4°), unsymmetrical triglycerides such as α-laurodistearin or α-stearodipalmitin had no measurable optical activity, although α-(*p*-nitrobenzoyl)-dibenzoin had $[\alpha]_D$ −20° (*cf.* also, Chapter X, p. 454). They pointed out that lack of observable rotation in the synthetic unsymetrical long-chain aliphatic triglycerides suggests that the same may apply in the natural compounds, and that natural unsymmetrical triglycerides, though they do not show measurable optical rotation, are not necessarily racemic. They further remarked that the slight evanescent rotation which has sometimes been recorded in the case of fats which have developed hydrolytic rancidity may be due to the presence therein of small amounts of optically active monoglycerides (produced in the course of partial enzymic hydrolysis).

Karrer *et al*[71] have recently suggested that the apparent optical inactivity of natural phytol may be due to a similar cause.

The small fully saturated glyceride contents of the fats dealt with on pp. 261–270. It may be pointed out, before discussing their compositions, that the minimal quantities of fully saturated components found in seed fats in which the ratio of saturated to unsaturated acids is approaching 2 : 1 is not, from one point of view, wholly in accordance with " even distribution " of *all* the fatty acids throughout the glycerol molecules. It certainly argues extremely even partition of the unsaturated and saturated acids, considered in these two groups ; but, in the cases which have just been discussed, where very frequently we encounter two different saturated acids (e.g. palmitic and stearic) and oleic acid all present in comparable proportions, it might be thought that complete even distribution should demand the presence of rather more than the observed small proportions of palmitostearins in addition to the palmito-oleins and stearo-oleins which are, in fact, usually present in quantity. In the particular group of fats which we are discussing, therefore, the avoidance of any marked quantity of fully saturated components (in other words, the almost complete association of oleic with saturated acids so as to produce glycerides in which, almost exclusively, oleic and saturated acyl groups are simultaneously present) is from one standpoint rather the " even distribution " of unsaturated with saturated acids than " even distribution " of the whole of the major component acids concerned. On the other hand, it must be remembered that in this group of fats oleic acid always forms 40 per cent. or more of the total acids ; this prominence as a major component acid involves, on the principles of " even distribution," the consequence that nearly all the triglyceride molecules will contain at least one oleo-group—in other words, few triglyceride molecules will include three saturated acyl radicals.

The component acids of the fully saturated glycerides present in small proportions in the fats discussed on pp. 261–270. It was pointed out (p. 257) that, when the proportion of oleic acid, and therefore of oleo-glycerides, in a fat is small (e.g. the Palmæ seed fats, nutmeg butter, dika fats), the component acids of the fully saturated, major portion of the fat are present in much the same proportions as in the whole fat. In cases where the ratio of saturated to unsaturated acids in the whole fat falls within the range of 1–1·7 : 1, on the other hand, there is, more often than not, a marked tendency for the saturated acid of lower molecular weight to concentrate in the small amounts of fully saturated components present in such fats. The reason for this is at present obscure, and this state of affairs does not hold in every case ; but it is sufficiently usual to deserve notice here, and is illustrated by the data collected in Table 74.

A seeming analogy might be drawn between these general characteristics of seed fat fully saturated glycerides and of the relative degrees of unsaturation of the acids present in fats of aquatic animals. In the latter category, it is well recognised that the acids of lower molecular weight (i.e. of the C_{14} and C_{16} series) are the most saturated ; the ratio of saturated to unsaturated

TABLE 74. *COMPARISON OF THE (MOLAR) COMPOSITION OF THE SATURATED ACIDS IN THE WHOLE FAT AND THE FULLY SATURATED COMPONENTS OF SEED FATS CONTAINING* 1-1·7 *MOLS. SATURATED ACID PER MOL. UNSATURATED ACID*

SEED FAT	PERCENTAGE COMPOSITION OF SATURATED ACIDS IN THE WHOLE FAT				FULLY SATURATED COMPONENTS PER CENT. (MOL.)	SATURATED ACIDS PRESENT (PER CENT.)		
	C_{14}	C_{16}	C_{18}	C_{20}		C_{16}	C_{18}	C_{20}
Borneo tallow	2	35	63	—	4·5	57	43	—
,, ,,	—	31	67	2	5·1	56	44	—
Njatuo tallow	—	10	90	—	1·8	13	87	—
Cacao butter	—	41	59	—	2·5	66	34	—
Allanblackia Stuhlmannii	—	6	94	—	1·5	32	68	—
Pentadesma butyracea	—	10	90	—	3·0	25	75	—
Garcinia morella	1	14	84	1	2·7	39	61	—
,, *indica*	—	5	95	—	1·5	33	67	—
Dacryodes rostrata	—	22	75	3	1·8	17	83	—
Pulasan fat	—	5	55	40	1·5	—	81	19
Rambutan tallow	—	4	27	69	1·4	—	41	59
Shea butter	—	12	88	—	4·5	55	45	—
,, ,,	1	19	80	—	2·5	50	50	—
Mowrah fat	—	53	47	—	1·2	67	33	—
Neem oil	—	49	47	4	0·6	33	67	—
Hodgsonia capniocarpa	1	78	20	1	2·7	92	8	—

acids in each group declines sharply on ascending the series from C_{14} to C_{22} (indeed it is unusual to find more than traces of the saturated C_{20} or C_{22} acids). Again, sperm head oil and porpoise body oil (Chapter VII, p. 295), which contain unusually large amounts of lower saturated acids, have fully saturated components in which these acids are definitely concentrated. It is possible to account for these phenomena in the aquatic animal fats by considerations of hydrogenation or saturation processes in the animal tissues ; but at present it seems unlikely that a similar mechanism is operative in seed fat metabolism.

(*c*) SEED FATS IN WHICH UNSATURATED ACIDS PREDOMINATE (LIQUID SEED FATS)

A number of liquid seed fats have already been studied by means of preliminary resolution into fractions of differing mean unsaturation by crystallisation from acetone at low temperatures, and this technique will doubtless be extended to many other fats in this group in due course. Meantime, in other cases, a good deal of information has been obtained by indirect methods, including the qualitative examination of crystalline bromoglycerides from unsaturated oils (Chapter V, p. 228), the determination of tristearin in the completely hydrogenated fats (*cf.* this chapter, p. 239), or the investigation of a series of incompletely hydrogenated products of an oil (*cf.* p. 240).

An interesting and entirely different procedure, the selective adsorption of mixed unsaturated glycerides of different mean unsaturation by a column of activated alumina, has been employed in one instance—that of linseed oil.[66] This method may well prove useful when applied to other oils of the highly-unsaturated or " drying " type, although its utility for the less unsaturated fats, in which only linoleic and oleic acids are represented, seems at present to be limited.

Up to the present, and in the relatively few instances amenable to arithmetical " computation," it appears that the proportions of the main component glycerides in the more unsaturated fats are predictable within approximate limits from their fatty acid compositions by calculations on the lines illustrated earlier in this chapter (pp. 249–255). It is also interesting to note, in fats which contain oleic and linoleic acids as main components, the wide variation in the proportions (observed or " computed ") of the component glycerides consequent upon, frequently, comparatively simple alterations in the relative proportions of these two acids. Moreover, by reason of the general operation of the " rule of even distribution," it is needful for oleic acid to form 70 per cent. or more of the total fatty acids of an oil before triolein is present in it in any quantity. Thus it will be seen from references to individual fats that olive and teaseed oils are almost the only ones which contain triolein in quantity—and these to a much smaller degree than was formerly supposed, owing to the presence of maximal amounts of saturated dioleins and of linoleodioleins. Again, although groundnut oil differs from olive oil only in its higher proportion of linoleic acid in the unsaturated C_{18} acids, and in the presence of a few per cent. of higher saturated acids, the difference is amply sufficient to result in the absence of triolein from groundnut oil. Many of the well-known differences in appearance and properties between oils such as olive and groundnut are, in fact, obviously the consequence of these somewhat profound differences in the nature and proportions of their chief component glycerides.

In the notes which follow with reference to individual liquid seed fats, the order of treatment is from the less unsaturated (" non-drying ") oil to the most unsaturated of the " drying " oils.

Teaseed oil. This is very similar to the fruit-coat olive oil in its component acids (palmitic 7·6, oleic 83·3, linoleic 7·4 per cent., with fractional percentages of myristic, stearic, and arachidic acids). It contains only traces of fully saturated components, whilst its content of tri-C_{18} glycerides is close to the minimum possible.[6a, 6b] It therefore consists of about 70 per cent. of tri-unsaturated glycerides (probably about 50 per cent. triolein and 20 per cent. linoleodioleins), the remainder being almost wholly monopalmitodi-" oleins " with subordinate amounts of other monosaturated-di-" oleins " and of dipalmito-" olein."

Groundnut oil. The component acids are usually oleic ca. 55–60, linoleic ca. 20–25, palmitic ca. 7–8, and stearic, arachidic, behenic, and lignoceric acids amounting together to about 10 per cent. Containing negligible proportions of fully saturated components, it was shown by the progressive hydrogenation method [6c] to include 56–57 per cent. (almost the minimum possible quantity) of tri-C_{18} glycerides. Gunde and Hilditch,[60] employing an unusual modification of the acetone-crystallisation technique, isomerised (" elaidinised ") groundnut oil with selenium at 220° before separating the semi-solid product into several fractions by crystallisation from acetone ; the chief components were estimated to be palmito-(+other monosaturated)-oleolinoleins 45, linoleodioleins 24, triolein 19, palmito-(+other monosaturated)-dioleins 11, and mono-oleo-disaturated 1 per cent. (mol.).

Almond oil. Gunde and Hilditch [60] applied the method used in the case of groundnut oil to an almond oil, the component acids of which included myristic 1, palmitic 5, oleic 77 and linoleic 17 per cent. The component glycerides consisted approximately of palmito-(+myristo-)diolein 17, linoleodiolein 52, and triolein 31 per cent., in close accordance with the rule of " even distribution."

Rape oil. The component acids include 40–50 per cent. of erucic, the remainder being a mixture of oleic and linoleic acids with very small proportions (3–4 per cent. in all) of palmitic and higher saturated acids. From crystallisation studies of the completely hydrogenated oil, Amberger[43] deduced the absence of triolein or trierucin, and the probable presence of considerable amounts of oleodierucin. Hilditch and H. Paul,[42] as a result of examination of the oil by progressive hydrogenation, confirmed and extended Amberger's work, and concluded that, apart from about 6 per cent. of mixed palmito-oleo- (or linoleo-) erucins, the rape oil investigated contained about 50 per cent. of di-C_{18}-erucin and about 44 per cent. of mono-C_{18}-dierucin (the C_{18} acid being either oleic or linoleic) ; they considered that both α- and β-" oleo "-dierucins and α- and β-erucodi-" oleins " were probably present.

Cottonseed oil. Hilditch and Lea[1] showed in 1927 that, in spite of the presence of 25 per cent. of saturated acids in the total acids, less than 1 per cent. of fully saturated glycerides occurred in cottonseed oil (component acids: myristic 3, palmitic 20, stearic 1, arachidic 1, oleic 30, linoleic 45 per cent. wt.). By crystallisation of the completely hydrogenated oil,[6a] and later as the result of progressive hydrogenation of the oil,[6b] it was established that the tri-C_{18} glyceride content was only 25 per cent., a figure which indicates that practically the whole of the saturated acids are in the form of monopalmitodi-unsaturated glycerides (or other monosaturated glycerides).

Hilditch and Maddison[18b] separated a specimen of cottonseed oil (component acids: myristic 1·4, palmitic 23·4, stearic 1·1, arachidic 1·3, hexadecenoic 2·1, oleic 22·9, linoleic 47·8 per cent. wt.) into six fractions by crystallisation from acetone between 0° and —35° as follows :

Fractions :	A	B	C	D	E	F
Iodine value	38·3	57·0	97·0	107·9	124·7	134·0
Per cent. (mol.)	0·8	14·5	32·5	10·2	31·3	10·7
Component acids (per cent. wt.)						
Myristic	—	3·0	2·6	1·3	1·6	0·7
Palmitic	66·3	51·9	25·8	20·8	11·8	7·6
Stearic	1·6	3·3	2·0	—	—	—
Arachidic	—	1·5	1·1	—	—	—
Tetradecenoic	—	—	0·1	0·1	0·2	0·2
Hexadecenoic	—	1·9	1·1	2·4	2·3	3·7
Oleic	19·2	16·4	24·9	26·8	24·3	22·8
Linoleic	12·2	22·0	42·4	48·6	59·8	65·0

In the most soluble fractions E and F the molar ratio of linoleic to oleic acid approached, but did not exceed, 2·5 : 1. Thus, in the most unsaturated part of the oil, this ratio indicates less linoleic acid than that which would necessitate the presence of trilinolein. This circumstance, coupled with failure to obtain a fraction of higher unsaturation by further crystallisation of fraction F, was taken to indicate the occurrence of the maximum possible quantity of mixed oleo-linoleins in the tri-unsaturated glycerides. It was estimated that the cottonseed oil consisted of palmito-oleolinoleins 35–40, palmitodilinoleins over 20, tri-unsaturated glycerides (mainly oleodilinoleins) ca. 28, and oleo- or linoleo-disaturated glycerides ca. 12–13 per cent. (mol.). Although the tri-C_{18} glycerides thus approach the minimum figure indicated by the earlier progressive hydrogenation studies (above), the more detailed analysis also indicated the presence of 12–13 per cent. of mono-unsaturated disaturated glycerides. These glycerides probably contain one of the minor component saturated acids in addition to a palmitic and an unsaturated acid group. Palmitic acid (24·5 per cent. mol.) as a major component acid is likely to occur once in the majority of the triglyceride molecules of the oil; the minor saturated acid components (which together amount to 4 per cent. (mol.) of the total acids) will, however, not occur more than once in any molecule. The chances of one of these minor saturated groups being accompanied by a palmitic group in a tri-glyceride molecule (leading to a disaturated glyceride) are thus large.

The fraction C from this fat, which from its fatty acid composition appeared to be wholly made up of monosaturated di-unsaturated glycerides and to contain a very high concentration of monopalmitodi-unsaturated glycerides, was completely hydrogenated at a low temperature (65°) and the product crystallised in order to obtain a pure specimen of palmitodistearin, the melting and transition points of which showed it to be β-palmitodistearin.[18b, 65b] It was thus established that, in the monopalmitodi-unsaturated glycerides of cottonseed oil, the palmitic group is exclusively attached to the β- or central hydroxyl group of the glycerol.

Sesamé oil (component acids: palmitic 9, stearic 4, arachidic 1, oleic 46, linoleic 40 per cent. wt.). Progressive hydrogenation studies [6a] showed that the oil (which contains little or no fully saturated components) has only 69 per cent. of tri-C_{18} glycerides. The saturated acids must therefore, as in the previous instances, be present almost wholly as monosaturated (mainly palmito- or stearo-) di-" oleins," and over two-thirds of the fat will consist of mixed oleo-linoleins.

Niger seed oil (component acids: myristic 1·7, palmitic 5·0, stearic 2·3, oleic 39·4, linoleic 51·6 per cent. wt.). Vidyarthi and Mallya [62c] studied the component glycerides of this oil (from the seed of *Guizotia abyssinica*, Compositæ) by forming its bromo-additive compounds, separating the latter into fractions by crystallisation from alcohol, acetone, and petrol at 0°, and determining the component acids in each of the debrominated fractions; they found that the oil contained no fully saturated glycerides, and (from the tristearin content of the completely hydrogenated oil) that 75 per cent. of tri-C_{18} glycerides were present in the fat. From their results they gave the following composition for the fatty glycerides: oleodilinolein 40, linoleodiolein 30, palmito-oleolinolein 11, palmitodilinolein 6, stearo-oleolinolein 4, myristo-oleo-linolein 3, and 2 per cent. (mol.) each of myristodilinolein, stearodilinolein, and trilinolein.

Tobacco seed oil (component acids: myristic 1·8, palmitic 7·8, stearic 5·6, oleic 30·2, linoleic 54·6 per cent. wt.) has been similarly studied by Venkatarao *et al.*,[63b] who reported component glycerides as follows: oleodilinolein 35, palmito-oleolinolein 18, stearo-oleolinolein 11, palmitodilinolein 9, linoleodiolein 7, trilinolein 7, and stearodilinolein 6 per cent. (mol.), with minor amounts of myristo-unsaturated glycerides.

Soya bean oil. From the presence of only 75 per cent. of tristearin in the completely hydrogenated oil,[6a] it appears that the saturated acids are here also present as monopalmito- or monostearo-di-unsaturated glycerides;

with a mixture of about 25 per cent. oleic, 55 per cent. linoleic and 2–3 per cent. linolenic acids in the unsaturated acids, it may be considered very unlikely that any significant proportions of either of the simple triglycerides trilinolein or triolein should be present. Examination of the bromo-additive products of the glycerides of soya bean oil by Suzuki and Yokoyama[44] and by Hashi[45] revealed no indication of either of the simple tri-unsaturated glycerides, but indicated the presence of a number of mixed glycerides such as oleodilinolein, dioleolinolein, oleolinoleo-linolenin, and linoleo-linolenins.

Safflower seed oil (*Carthamus tinctorius*, Compositæ). The component glycerides of two specimens of this seed fat have been reported by Indian investigators. Vidyarthi,[62d] using the same methods as he applied to niger seed oil (above) found oleodilinolein 64, linoleodiolein 15, palmitodi-unsaturated 11, stearo-di-unsaturated 3, myristo-di-unsaturated 4, and trilinolein 3 per cent. (mol.) in a safflower oil, the component acids of which were myristic 2, palmitic 3, stearic 1, oleic 32, linoleic 61, and linolenic 1 per cent. (wt.).

Lagawankar *et al.*,[68] for an oil with closely similar component acids (palmitic 2, stearic 2, arachidic 1, oleic 38, and linoleic 57 per cent. wt.) gave a very different composition: trilinolein 45, monosaturated-oleo-linoleins 18, linoleodiolein 15, and triolein 8 per cent. The presence of so much trilinolein and triolein seems doubtful, and, judging from the results for component glycerides of other seed oils of a similar nature (above) it would appear that Vidyarthi's conclusions [62d] are probably nearer the truth.

Linseed oil. The component glycerides of this important oil have not yet been satisfactorily determined on a quantitative basis. The content of tri-C_{18} glycerides (83 per cent., determined as tristearin in the completely hydrogenated fat [6a]) is not much greater than the minimum possible (81 per cent.), and it may be accepted therefore that the 10 per cent. of saturated acids are substantially all in combination as monosaturated-di-unsaturated glycerides. Much the same will probably apply to oleic acid, present in somewhat similar proportions.

Qualitative information obtained by crystallisation of the bromo-adducts of linseed oil glycerides by Eibner [4] and his colleagues enabled these workers to identify two linoleodilinolenins and an oleodilinolenin in linseed oils from India, Riga, and Argentina; whilst Suzuki and Yokoyama,[46] using similar methods, have reported the presence in linseed oil of two linoleodilinolenins, a dilinoleo-monolinolenin, and an oleodilinolein.

Selective adsorption on a column of activated alumina has been employed by Walker and Mills [66] to effect a separation of the mixed glycerides into simpler mixtures of varying mean unsaturation, the more unsaturated components being adsorbed preferentially in the upper parts of the column. By this means, these investigators were able, in the first instance, to determine approximately the proportions of triglycerides in linseed oil which contained respectively 7, 6, 5 or 4 ethenoid groups. For typical oils of La Plata or Calcutta origin, they found about 63–64 per cent. of glycerides containing 7 ethenoid groups, 15–20 per cent. with 6, 9–10 with 5, and 5–8 with 4 ethenoid groups. The possible combinations of acids in each of these classes are as follow:

7: Oleodilinolenin, linolenodilinolein.

6: Monosaturated-dilinolenin, trilinolein, oleolinoleo-linolenin.

5 : Monosaturated-linoleo-linolenin, linolenodiolein, oleodilinolein,
4 : Monosaturated-dilinolein, monosaturated-oleolinolenin, linoleodiolein.

Later, these workers showed that, by repeated adsorption on fresh columns of alumina of the 63–64 per cent. of primarily separated glycerides with a mean unsaturation of 7 ethenoid groups, it was possible to isolate some material with an average content of 8 ethenoid groups per triglyceride molecule (linoleodilinolenin), and a very small proportion of glycerides with 9 ethenoid groups per molecule (trilinolenin) ; whilst no evidence of glycerides with less than 4 ethenoid groups per molecule was forthcoming from the 5–8 per cent. of least unsaturated primary fractions.

This work thus shows that linseed oil, with an average fatty acid composition of linolenic 50–55, linoleic 20–25, oleic 10–15, and saturated 10 per cent., is composed, to the extent of about two-thirds of the total glycerides, of compounds containing two, and frequently three, di- or tri-ethenoid acyl groups. It also indicates that the usual rules of " even distribution " apply in the case of linseed oil, the major component acids (linoleic and linolenic) occurring once, and often twice, in most of the triglyceride molecules, whilst the less abundant oleic, palmitic, and saturated acids contribute only one group to any triglyceride molecule, so far as this evidence goes. Probably about 50 per cent. of linseed oil consists of mixed linoleo-linolenins, the remaining 50 per cent. containing, for the most part, one saturated or one oleic group and two polyethenoid acyl groups.

The circumstance that very few of the triglyceride molecules will contain less than two di- or tri-ethenoid acyl groups doubtless accounts to a large extent for the specifically good " drying " properties of linseed oil films.

Other unsaturated seed fats. A specimen of *chaulmoogra oil* (component acids: hydnocarpic 59 and chaulmoogric 40 per cent.) was fractionally crystallised after complete hydrogenation by Bömer and Engel,[47] who were able to separate the hydrogenated product into 79 per cent. of dihydrochaulmoogro-di-dihydrohydnocarpin and 13 per cent. of dihydrohydnocarpo-di-dihydrochaulmoogrin ; these figures accord well with complete partition of the two acids in the form of " evenly distributed " mixed glycerides.

Tung oil and *oiticica oil*, the component acids of which contain respectively about 80 per cent. of α-elæostearic acid and about 70 per cent. of α-licanic (keto-elæostearic) acid, were converted into their crystalline " β "-isomerides by Morrell and Davis.[11] They found that the crystalline " β-elæostearin " from tung oil was almost pure tri-β-elæostearin, whereas the " β-licanin " from oiticica oil contained but little tri-β-keto-elæostearin, and was mainly a mixture of glycerides in which two keto-elæostearic groups were associated with one saturated, or non-conjugated unsaturated, acyl group. These observations indicate that the glycerides of these two oils are assembled on the same general principles as those of the great majority of the seed fats which have been dealt with in this chapter.

FRUIT-COAT FATS

It was shown in Chapter IV (p. 148) that the outstanding characteristic of fruit-coat fats is that their major component acids are confined to palmitic, oleic, and linoleic acids, irrespective of the component acids of the corresponding seed fats or of the botanical families to which the parent plants belong. The data in Table 62 and Fig. 2 of this chapter (pp. 234, 235) indicate that, so far as content of fully saturated glycerides (in these cases always substantially tripalmitin) is concerned, some fruit-coat fats follow the same course as almost all seed fats, i.e. fully saturated glycerides only appear in excess of the proportions of saturated acid required to associate with unsaturated acids (ca. 1·5 : 1) in the form of mixed saturated-unsaturated triglycerides. This holds for Stillingia tallow, piqui-a pericarp fat, and the fruit-coat fat of *Dacryodes rostrata* (Java almond).

On the other hand, the fruit-coat fats which happened first to be studied by the oxidation method—palm oil, olive oil, laurel berry pericarp fat—show definitely higher (albeit still small) contents of fully saturated components than would be expected according to the usual generalisation. This led at first to the belief that the mixed glycerides of fruit-coat fats were constituted essentially differently from those typified by the seed fats. Subsequently, not only were the above-mentioned instances of conformity with the usual habit encountered, but study of the mixed saturated-unsaturated glycerides of olive and palm oils showed that, apart from the observed somewhat abnormal proportions of tripalmitin, the whole of each of these fats was assembled on the usual, " evenly distributed " lines. Whilst, therefore, as pointed out on p. 236, it is hardly possible to say at present whether the strictly " evenly distributed " type, or the slightly abnormal type, of fruit-coat fat is the more common in this group, it may perhaps be suggested that the occasional presence in a fruit-coat fat of more tripalmitin than would be expected may be somewhat analogous to the production, in certain seed fats, of small quantities of saturated components in which palmitic acid is frequently concentrated to a greater extent than in the saturated acids of the bulk of the fats in question.

Some account will now be given of the few instances of fruit-coat fats, the glyceride structure of which has been investigated in detail.

Sumach berry fat. The fat present in the exterior of berries of *Rhus* species is technically called " Japan wax," owing to its hardness, which is due to the presence of much tripalmitin. It is a mixture of glycerides of the following component acids (Tsujimoto [48]) : palmitic 77, stearic 5, oleic 12, and saturated dicarboxylic acids of the C_{22} and C_{23} series, 5–6 per cent. (wt.). The high content of tripalmitin is a consequence of its fatty acid composition, whilst the long-chain dicarboxylic acid components confer certain specific physical properties on the fat.

Stillingia tallow. This is a fatty deposit on the pericarp of the seeds of *S. sebifera*, the seeds containing a liquid fat rich in linoleic and oleic acids. Hilditch and Priestman [49] examined two specimens of Stillingia tallow with the following results :

(*a*) *United States* (*Florida*) *plantation fat:* Component fatty acids: lauric (?) 1·2, myristic 2·9, palmitic 63·1, stearic 3·2, oleic 29·6 per cent. (wt.). Fully saturated glycerides, 27·6 per cent. (wt.) ; (component acids : myristic 7·2, palmitic 83·0, and stearic 9·8 per cent. wt.).

The fully saturated glyceride content indicated that the fat must have contained between 61 and 66·5 per cent. of mono-oleo-disaturated glycerides, whilst monoazelaodipalmitins equivalent to a content of over 41 per cent. of oleodipalmitin in the original fat were isolated from the acidic products of oxidation by crystallisation.

(*b*) *Chinese native fat:* Component fatty acids: lauric (?) 2·5, myristic

3·6, palmitic 57·6, stearic 1·8, oleic 34·5 per cent. (wt.); fully saturated glycerides, 23·6 per cent. (wt.).

The result of these experiments is thus to indicate that the greater part (over 60 per cent.) of Stillingia tallow is composed of mono-oleo-disaturated glycerides, whilst fully saturated glycerides are present to the extent of about 25 per cent. or more. Since palmitic acid forms nearly 90 per cent. of the saturated fatty acids, these respective classes of glycerides must consist mainly of oleodipalmitins and tripalmitin.

Klimont[50] had concluded many years earlier, as a result of fractional crystallisation of the fat itself, that oleodipalmitin, m.p. 37°, was an important component. It appears probable, from the melting point of the natural oleodipalmitin, that only the β-oleodipalmitin is present and that selective configuration of the glyceride occurs in this, as in some seed, fats.

Palm oils. Most of those who make technical use of the red palm oils of *Elæis guineensis* have long since realised that the statement—still occasionally found in the literature—that these oils contain tripalmitin in abundance is far from the truth. Nevertheless, they contain more of this simple triglyceride than would be expected from their fatty acid composition, if the palm oil glycerides were entirely of the " evenly distributed " type which is so characteristic of seed fats (and of some fruit-coat fats). From crystallisation of a palm oil and of the same oil after it had been hydrogenated, Brash[51] concluded that there was about 10 per cent. of tripalmitin present, and also, probably, about the same proportion of triolein. Hilditch and (Miss) E. E. Jones[52] isolated and examined the fully saturated glycerides from Belgian Congo and Malaya plantation oils and from Cameroons and Drewin (Ivory Coast) native oils with the following results:

	Component Acids of the Oil					Fully Saturated Glycerides			
							Component Acids		
	Myristic	Palmitic	Stearic	Oleic	Linoleic		Myristic	Palmitic	Stearic
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Belgian Congo	1·2	43·0	4·4	40·2	11·2	9·9	3	86	11
Malaya	2·5	40·8	3·6	45·2	7·9	9·1	5	90	5
Cameroons	1·4	40·1	5·5	42·7	10·3	7·9	7	81	12
Drewin	1·4	32·7	7·5	51·7	6·7	7·0			

The amount (7–10 per cent.) of fully saturated components varies according to the ratio of saturated to unsaturated acids in the fat as a whole; 70–80 per cent. of the fully saturated glycerides consists of tripalmitin. These results indicate that palm oils consist mainly of " oleo "-dipalmitins and palmitodi-" oleins."

Steger and van Loon[53] found only 2 per cent. of fully saturated glycerides (m.p. 54–55°—impure tripalmitin and/or palmitostearins) in a Sumatra plantation palm oil of the " Buitenzorg " variety, the component acids of which were myristic 1·5, palmitic 42·9, stearic 4·7, oleic 39·8, and linoleic 11·3 per cent. (wt.).

Subsequently, Banks, Dean, and Hilditch[41] determined the tristearin content of completely hydrogenated palm oils, and also studied their progressive hydrogenation in the cases of a Belgian Congo plantation oil and a Cape Palmas native oil (component acids, respectively: myristic 1·3, 1·6; palmitic 41·4, 32·3; stearic 4·7, 5·5; oleic 42·9, 52·4; linoleic 9·7, 8·2 per cent. wt.). They reached the following estimates for the chief component glycerides of the two palm oils:

COMPONENT GLYCERIDES	BELGIAN CONGO PLANTATION OIL PER CENT. (MOL).	CAPE PALMAS NATIVE OIL PER CENT. (MOL.)
Fully saturated	6·5	3·5
(including tripalmitin	ca. 5·5	ca. 2)
"Oleo"-dipalmitins	29·5	16·5
Palmitodi-"oleins" (together with any "oleo"-palmitostearin)	58	66
Tri-C_{18} glycerides (tri-"oleins" or stearodi-"oleins")	6	14

Later, Hilditch and Maddison [18a] studied the component glycerides of a Cameroons plantation palm oil and of a Bassa native palm oil by examination of the fractions of each fat obtained by preliminary systematic crystallisation from acetone. The presence of subordinate amounts of fully unsaturated glycerides (probably linoleodiolein) as well as of fully saturated glycerides was demonstrated, and the complete data for each of these fats are shown in Table 75, together with data computed from the composition of the total fatty acids by Hilditch and Meara [59a] (*cf.* pp. 251, 254).

TABLE 75. *COMPONENT ACIDS AND GLYCERIDES (PER CENT. MOL.) OF PALM OILS* [18a, 59a]

CAMEROONS PLANTATION OIL

Component acids	
Myristic	1·3
Palmitic	47·3
Stearic	3·9
Hexadecenoic	0·8
Oleic	36·8
Linoleic	9·9

	FOUND	"COMPUTED" (i)	"COMPUTED" (ii)
Component glycerides			
Tripalmitin	5	4	—
Dipalmitostearin	3	3	—
"Oleo"-dipalmitin	43	43	48
"Oleo"-palmitostearin	11	8	11
Palmitodiolein	32	12	10
Palmitolinoleo-olein		22	28
Linoleodiolein	6	8	3

BASSA NATIVE OIL

Component acids	
Myristic	0·7
Palmitic	39·8
Stearic	3·6
Hexadecenoic	1·5
Oleic	48·2
Linoleic	6·2

	FOUND	"COMPUTED" (i)	"COMPUTED" (ii)
Component glycerides			
Tripalmitin	3	2	—
Dipalmitostearin	3	2	—
"Oleo"-dipalmitin	31	30	31
"Oleo"-palmitostearin	10	6	7
Palmitodiolein	41	41	43
Palmitolinoleo-olein		7	13
Linoleodiolein	12	12	6

(i) Fully saturated and tri-unsaturated glycerides computed as described below (p. 283); in remainder of acids, oleic proportioned between palmitic, stearic, and linoleic.

(ii) Oleic acid proportioned between palmitic, stearic, and linoleic.

The further evidence obtained by the crystallisation procedure[18a] on the whole confirms that which resulted from progressive hydrogenation studies.[41] The data for the Cameroons plantation and the Bassa native oils may, in fact, be taken as characteristic for palm oils of their respective fatty acid compositions, and a general statement of the glycerides present in commercial palm oils may be made as follows :

The chief components of palm oils are " oleo "-dipalmitin and palmitodi-" olein," in amounts which vary according to the proportions of palmitic, oleic and linoleic acids in the whole fats. Together, these two groups of glycerides usually amount to 70–75 per cent. of palm oil, " oleo "-dipalmitin preponderating in oils with high palmitic acid content, and conversely. The other (minor) components are about 10–15 per cent. of " oleo "-palmitostearin ; linoleodiolein (with possibly a very little triolein), 6–15 per cent., according to the oleic and linoleic acid content of the palm oil ; and about 3–9 per cent. of tripalmitin+dipalmitostearin, varying with the palmitic acid content of the palm oil.

The most common types of plantation or of native Lagos, Nigeria, Cameroons, etc., palm oils will usually be composed of about 45 per cent. " oleo "-dipalmitins, about 30 per cent. palmitodi-" oleins," about 10 per cent. of " oleo "-palmitostearins, and about 6–8 per cent. each of linoleodiolein and fully saturated glycerides (tripalmitin+dipalmitostearin). The semi-solid nature of palm oil at ordinary European temperatures is due to the presence of the solid mono-" oleo "-glycerides (with the small amount of fully saturated components) dispersed through the palmitodi-" oleins " (mainly still liquid at this temperature).

Since palm oils exhibit some departures from the strict rule of " even distribution," computation of their component glycerides based on partition of their oleic acid contents amongst the remaining component acids (palmitic, stearic, linoleic) fails to give a complete reproduction of the observed facts, especially as regards the fully saturated and completely unsaturated triglycerides of the oil. As in some similar instances in other fats (*cf.* pp. 254, 256), a more exact replica of the experimental findings is arrived at in palm oils in the following manner. From the cubes of the percentages of saturated and unsaturated acids in the palm oil may be obtained the approximate contents of fully saturated and tri-unsaturated glycerides if these were respectively produced according to " random " distribution. (In the case of the Cameroons oil in Table 75, with 52·5 per cent. saturated and 47·5 per cent. unsaturated acids, this would give 14 per cent. of fully saturated and 11 per cent. of tri-unsaturated glycerides.) The " computed " fully saturated glyceride content is taken as half of this amount, and assumed to consist of equal amounts of tripalmitin and dipalmitostearin, up to a maximum content of 3 per cent. of the latter. The tri-unsaturated glyceride content is also taken as half of the amount calculated by " random " distribution, and as linoleodiolein. The proportions of the individual acids in the fully saturated and tri-unsaturated glycerides are deducted from the total amounts of each fatty acid, and the remaining oleic acid is partitioned in the usual way (p. 250) amongst the remaining palmitic, stearic, and linoleic acids (in the course of which a little more linoleodiolein may appear).

It is believed that by this means the approximate composition of palm oil glycerides can be deduced with reasonable accuracy from a component fatty acid analysis.

Piqui-a pericarp fat. The fruit-coat fat of *Caryocar villosum* is interesting because its fatty acids closely resemble those of palm oils, namely: myristic 1·5, palmitic 41·2, stearic 0·8, oleic 53·9, linoleic 2·6 per cent. (wt.). Hilditch and Rigg [36] found that it contained only 2 per cent. of fully saturated components (tripalmitin), thus differing somewhat from palm oils of similar fatty acid composition. No tristearin was detected in the completely hydrogenated fat and the components of the fat (in addition to 2 per cent. of tripalmitin) are therefore 42 per cent. of oleodipalmitins and 56 per cent. of palmitodioleins—an instance of pronounced "even distribution."

Fruit-coat fat of Java almond (*Dacryodes rostrata*). This fat, examined by Hilditch and Stainsby,[31*] is also of the completely evenly distributed type. Its component acids are similar to those of the more unsaturated variety of palm oil (e.g. the Cape Palmas oil above), and comprise palmitic 33·9, stearic 2·7, oleic 59·3, and linoleic 4·1 per cent. (wt.). Palmitodi-" oleins" probably form nearly 85 per cent. of the fat, which further contains about 14 per cent. of "oleo-" dipalmitins and less than 1 per cent. of fully saturated glycerides (palmitostearins).

Laurel pulp oil (*Laurus nobilis*). This liquid fruit-coat fat (component acids: lauric 2·7, palmitic 20·3, oleic 63·0, linoleic 14·0 per cent. wt.) was found by Collin [24b] to contain 3 per cent. of fully saturated glycerides (substantially tripalmitin). It may be contrasted with cottonseed oil, which has almost the same quantity of combined palmitic acid, but which yields no appreciable quantity of fully saturated components. The high content of trilaurin in the corresponding laurel kernel fat (p. 260) is much more exceptional than the tripalmitin content of the pulp fat, which is in line with fruit-coat fats of the palm and olive oil type.

Olive oil. This important fruit-coat fat, the component acids of which include about 12 per cent. of saturated acids (mainly palmitic), nearly 80 per cent. of oleic acid, and about 8 per cent. of linoleic acid (wt.), contains 2 per cent. of fully saturated glycerides [8a] (tripalmitin); this amount is definitely larger than is usually observed in a seed fat of similarly low saturated acid content. Progressive hydrogenation studies [6b] have shown, in Tuscany and Palestine olive oils, that the tri-C_{18} glyceride content is very near the minimum consistent with the fatty acids present.

It has been mentioned (Chapter IV, p. 151) that two types of olive oil occur. In the most common variety, oleic acid forms 75 per cent. or somewhat more of the component acids with about 10 per cent. of palmitic and somewhat less linoleic acid; in the other, apparently rarer, type the component acids include about 15 per cent. each of palmitic and linoleic with 65 per cent. or less of oleic acid. Hilditch and Maddison [18c] have investigated, by separating each oil into six fractions by crystallisation from acetone at temperatures down to —30°, the component glycerides of a Turkish olive oil of the normal type, and an unusual Italian olive oil of the less common type, with the following results.

Turkish olive oil. Component acids: myristic 0·5, palmitic 10·0, stearic 3·3, arachidic 0·1, hexadecenoic 1·0, oleic 76·5, linoleic 8·6 per cent. (wt.). Chief component glycerides (approximate): monosaturated-dioleins 45, triolein 30, and monolinoleo- (or hexadeceno-) dioleins 25 per cent. (mol.).

Italian olive oil. Component acids: myristic 1·2, palmitic 15·6,

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[*] Published erroneously as the fruit-coat fat of *Sterculia fœtida.*

stearic 2·0, hexadecenoic 1·6, oleic 64·6, and linoleic 15·0 per cent. (wt.). Chief component glycerides (approximate): monosaturated-dioleins 55, monolinoleo- (or hexadeceno-) dioleins 35, monosaturated-oleo-linoleins 5, and triolein 5 per cent. (mol.).

The content of fully saturated glycerides in both these olive oils was found to be lower than that stated above (less than 0·5 per cent. in the Turkish oil, and only traces in the Italian oil).

The frequent statement that olive oil consists almost entirely of triolein is thus by no means accurate; it is unlikely that the simple triglyceride triolein ever forms more than half of the glycerides present in olive oil. Perhaps more important than the actual content of triolein is the proportion of the olive oil made up of glycerides in which a linoleic group is present. Linoleo-glycerides are far more susceptible than oleo-glycerides to atmospheric oxidation, and the content of these glycerides in an olive oil is therefore significant in relation to its suitability either for edible purposes (e.g. salad oil or packing oil for fish, etc.) or for use in the textile industries. The olive oils of the more common type will contain about 25 per cent. of linoleo-glycerides, whereas these may form 40 per cent. or more of the alternative, but less common, variety of genuine olive oil.

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CHAPTER VII

THE COMPONENT GLYCERIDES OF ANIMAL FATS

DETAILED modern work on the glyceride structure of animal fats has been so far chiefly concerned with depot and milk fats of the herbivorous land animals, especially those of ox, sheep, and pig depots and cows' milk. Depot fats of a few of the smaller animals and birds have been similarly investigated but, although the general outlines of animal depot fat structure are probably now well understood, the range of investigation has been more restricted than is the case with vegetable seed fats. This is of course natural, owing to the present lack of data for even the component acids of many groups of land animals, especially the carnivora (*cf.* Chapter III, p. 85). Modern research on the component glycerides of marine animal fats is not lacking, but in this field the large number of component acids present, and the highly unsaturated nature of many of these, has so far restricted the application of the methods which have proved useful when the major constituent acids of a fat are only three or four in number, and when unsaturation is practically confined to acids of the C_{18} series (usually oleic and linoleic). We shall consider in sequence the available data regarding the component glycerides of marine animal fats, and those of land animal fats. (The component acids of these fats were dealt with respectively in Chapters II and III.)

MARINE ANIMAL FATS

The great majority of fish oils and of ordinary whale, seal, and similar oils contain only about 15–20 per cent. of saturated fatty acids, and consequently most of them possess no detectable quantity of fully saturated components. The oxidation method of investigation is therefore not of great service when applied to these fats, although it has given useful information with regard to the rather special case of the sperm whale oils (or rather waxes), to which further reference is made later.

The structure of the glycerides of many marine animal oils is nevertheless well illustrated, from a qualitative point of view, by the studies of Suzuki and his co-workers.[1] They established the presence of a sufficient number of mixed glycerides in these oils to justify the conclusions that the distribution of the numerous component acids of a fish or whale oil amongst the glycerol molecules of the fat is profoundly heterogeneous and that, whilst simple triglycerides are either absent or very rare, the most common form is a triglyceride containing three different acids, although sometimes two radicals of the same fatty acid are observed in a single glyceride molecule. The following examples of glycerides isolated in the form of their bromo-addition products by Suzuki and co-workers from various oils will serve by way of illustration :

Cod liver oil : stearidono-diclupanodonin, diarachidono-clupanodonin, hexadeceno-stearidono-clupanodonin, hexadeceno-arachidono-clupanodonin, dihexadeceno-linolenin and -linolein, etc.

Herring oil : hexadeceno-diarachidonin, gadoleo-diarachidonin, linoleno-gadoleo-clupanodonin, linoleo-digadolein and -dihexadecenoin, dicetoleo-gadolein, etc.

Sardine oil : some of the foregoing, with dicetoleo-olein, dicetoleo-arachidonin, triolein, triarachidonin, etc.

Shark liver oil : linoleno-diclupanodonin, arachidono-diclupanodonin, linoleno-arachidono-clupanodonin, linoleno-digadolein, dihexadeceno-linolein, palmito-diolein, triolein, etc.

Whale oil : oleo-arachidono-clupanodonin, oleo-diclupanodonin, oleo-diarachidonin, dihexadeceno-olein, etc.

Confirmatory evidence of the very mixed character of whale oil glycerides is afforded by the work of Greitemann [2] who isolated specimens of the following mixed glycerides from hydrogenated whale oil: myristo-palmito-arachidin (m.p. 49·5°), palmito-stearo-arachidin (m.p. 57·3°), distearo-arachidin (m.p. 62·3°), stearo-arachido-behenin (m.p. 65°) and traces of diarachido-behenin and arachido-dibehenin.

The glycerides of *cod liver oil* and of an *Antarctic whale oil* were studied by means of catalytic hydrogenation to varying stages by Harper and Hilditch [3] and by Hilditch and Terleski.[4] In the earlier stages of hydrogenation of these oils the highly unsaturated (C_{20} and C_{22}) acyl groups are chiefly reduced, but subsequently palmitic and stearic groups are formed from the corresponding mono-ethenoid glycerides whilst a certain proportion of di- or tri-ethenoid C_{20} and C_{22} compounds are still present. Even at low iodine values, e.g. 20–30, of the hydrogenated fats, some of the C_{20} and C_{22} acids are still more highly unsaturated than mono-ethenoid. The rate of production of fully saturated glycerides is slow until the final stages of the reduction (below iodine value 40–50). A summary of the data obtained for the component acids of the hydrogenated fats and also for the fully saturated glycerides produced is given in Tables 76 (cod liver oil) and 77 (Antarctic whale oil) ; the amounts of the component acids in the fully saturated glycerides are those present in 100 mols. of the hydrogenated fat (and not their percentage composition), in order to display more clearly the progressive changes in the nature of the fully saturated glycerides in relation to the hydrogenated fats as a whole.

The figures in Tables 76 and 77 show that in both the fish oil and the marine mammal blubber oil the fully hydrogenated triglycerides at first produced by hydrogenation contain chiefly palmitic and stearic (and myristic) acids, arachidic and behenic acids being present only in small proportions. Subsequently saturated glycerides containing the latter are produced in quantity, whilst palmitic and stearic glycerides are being formed at the same time. This is further evidence that the original oils consist of a complex mixture of mixed triglycerides in which many combinations of the component acids are present, and in which there are always at least two, and usually three different acids in each triglyceride.

In cod liver oil, which contains 45 per cent. of unsaturated acids of the C_{20} and C_{22} series, most of the glyceride molecules will contain at least one acyl group from these series. In the whale oil, the mixture of glycerides is probably almost as complex but, owing to the presence of only 16–20 per cent. of unsaturated C_{20} and C_{22} acids, almost half of the oil prob-

TABLE 76. *COMPOSITION OF ORIGINAL AND HYDROGENATED COD LIVER OILS (MOL. PER CENT.)*

Iodine value of fat:	177·7*	100·3	77·0	63·0	48·8	35·8	24·8	14·3
Component acids:								
Saturated:								
C_{14}	1·8	4·0	3·0	3·8	1·8	2·2	2·9	3·8
C_{16}	14·0	13·9	15·6	17·5	21·2	22·2	21·4	22·9
C_{18}	1·5	3·8	9·0	11·5	15·3	16·4	20·7	22·7
C_{20}	—	1·7	3·9	5·4	9·0	13·0	16·5	21·3
C_{22}	—	0·6	2·3	2·9	4·9	8·4	12·1	13·9
C_{24}	—	0·4	0·1	0·2	0·3	0·2	0·5	0·3
Unsaturated:								
C_{14}	2·1	—	0·1	0·9	1·3	0·8	0·4	0·3
C_{16}	9·3	7·8	7·2	5·3	2·7	3·1	2·4	0·5
C_{18}	26·4	23·1	18·0	16·8	13·0	10·5	6·4	2·4
C_{20}	25·8	24·3	21·1	16·5	13·4	12·7	7·6	5·7
C_{22}	19·1	20·4	19·0	18·7	16·5	10·3	8·6	5·3
C_{24}	—	—	0·7	0·5	0·6	0·2	0·5	0·9
Mean unsaturation of unsaturated acids:								
C_{14}	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)
C_{16}	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)
C_{18}	(−3·3)	(−2·2)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)
C_{20}	(−5·5)	(−3·6)	(−2·8)	(−2·5)	(−2·3)	(−2·2)	(−2·3)	(−2·0)
C_{22}	(−7·4)	(−4·3)	(−3·5)	(−3·0)	(−2·7)	(−2·6)	(−2·5)	(−2·4)
Fully saturated glycerides			4·9	10·4	15·7	22·0	46·2	60·4
Component acids in fully saturated glycerides:								
Myristic				0·4	0·5	1·2	2·9	1·3
Palmitic				3·1	6·1	6·7	12·2	17·6
Stearic				3·4	4·6	5·2	13·8	15·9
Arachidic				2·7	3·0	5·8	10·6	15·2
Behenic				0·8	1·0	2·3	6·7	9·5
Lignoceric				—	0·5	0·8	—	0·9

* Original oil.

ably consists of glycerides containing only acids of the C_{18}, C_{16}, and C_{14} series.

A hydrogenated whale oil of similar iodine value to beef or mutton tallow contains about the same proportion of fully saturated glycerides as the latter, and, in consequence of the relative lack of C_{20} or C_{22} saturated acids at the earlier stages of hydrogenation, the component acids of such fully saturated glycerides are more similar to those of the corresponding components of tallows than might at first be expected. The (liquid) components of the rest of the fat (mixed saturated-unsaturated glycerides) are of course entirely different from those of tallow, owing to the presence of C_{20} and C_{22} unsaturated acids and of the "*iso*"-unsaturated acids of hydrogenation.

An Antarctic whale oil was separated by crystallisation from acetone between −10° and −30° into four fractions by Hilditch and Maddison,[39] and the component acids determined in each fraction and in the whole fat. The molar percentages and mean unsaturation of the acids in each group are shown in Table 78.

Although the component acids in each fraction were still too complex to

TABLE 77. *COMPOSITION OF ORIGINAL AND HYDROGENATED ANTARCTIC WHALE OILS (MOL. PER CENT.)*

Iodine value of fat:	109·3*	88·6	70·7	48·8	28·2	11·9
Component acids:						
Saturated:						
C_{14}	7·5	9·9	10·6	11·1	11·2	12·8
C_{16}	19·3	17·1	17·9	25·6	30·2	29·2
C_{18}	2·3	2·6	2·3	10·4	20·8	32·3
C_{20}	—	0·2	0·2	2·6	6·1	9·5
C_{22}	—	—	—	0·3	1·6	3·4
Unsaturated:						
C_{14}	4·4	2·4	3·6	2·2	1·8	0·7
C_{16}	14·2	17·5	16·3	8·2	3·7	1·3
C_{18}	37·0	33·7	32·9	25·9	15·1	6·4
C_{20}	10·1	13·2	11·1	9·5	6·3	3·0
C_{22}	5·2	3·4	5·1	4·2	3·2	1·4
Mean unsaturation of unsaturated acids:						
C_{14}	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)
C_{16}	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)	(−2·0)
C_{18}	(−2·6)	(−2·2)	(−2·0)	(−2·0)	(−2·0)	(−2·0)
C_{20}	(−5·6)	(−4·4)	(−3·2)	(−2·4)	(−2·2)	(−2·0)
C_{22}	(−9·0)	(−6·9)	(−3·8)	(−2·7)	(−2·3)	(−2·0)
Fully saturated glycerides			4·7	13·7	32·0	64·4
Component acids in fully saturated glycerides:						
Myristic			1·9	2·3	6·5	11·1
Palmitic			1·9	6·5	12·0	21·4
Stearic			0·9	3·9	10·0	21·8
Arachidic			—	1·0	2·7	7·3
Behenic			—	—	0·8	2·8

* Original oil.

TABLE 78. *COMPONENT ACIDS OF ANTARCTIC WHALE OIL AND OF FRACTIONS SEPARATED BY LOW-TEMPERATURE CRYSTALLISATION (MOL. PER CENT.)*

	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
I. *Whole fat*						
Saturated	0·3	11·0	16·6	2·7	0·2	—
Unsaturated	—	3·0	15·4	33·8	12·0	5·0
Mean unsaturation	—	−2·0	−2·0	−2·6	−5·6	−9·0
II. *Fractions separated by crystallisation*						
A. *Insoluble at* −10° (9·5 per cent.)						
Saturated	1·4	23·0	36·4	3·8	—	—
Unsaturated	—	1·3	6·2	25·7	2·2	—
Mean unsaturation	—	−2·0	−2·0	−2·0	−4·0	—
B. *Soluble at* −10°, *insoluble at* −20° (38·1 per cent.)						
Saturated	0·1	12·9	18·6	2·3	0·4	—
Unsaturated	—	3·0	14·5	38·3	8·5	1·4
Mean unsaturation	—	−2·0	−2·0	−2·1	−5·0	−10·0
C. *Soluble at* −20°, *insoluble at* −30° (6·3 per cent.)						
Saturated	1·7	5·9	8·8	—	—	—
Unsaturated	—	5·2	18·5	44·9	15·0	—
Mean unsaturation	—	−2·0	−2·0	−2·3	−7·5	—
D. *Soluble at* −30° (46·1 per cent.)						
Saturated	0·2	7·6	11·7	3·0	—	—
Unsaturated	—	3·0	17·6	30·4	16·7	9·8
Mean unsaturation	—	−2·0	−2·2	−3·0	−9·0	−10·2

permit of any definite allocation of component glycerides, consideration of the various groups of acids present in each fraction led to an estimate of the general composition of its glycerides, from which it appeared that the probable components of the whole whale oil were made up somewhat as follows :—

PER CENT. (MOL.)	ACID GROUPS PRESENT
66	1 unsaturated C_{18}, 1 saturated, 1 unsaturated C_{14}, C_{16}, C_{20} *or* C_{22}.
12	1 unsaturated C_{18}, 2 unsaturated C_{14}, C_{16}, C_{20} *or* C_{22}.
8	1 unsaturated C_{18}, 1 myristic, 1 palmitic.
6	2 unsaturated C_{18}, 1 saturated.
4	3 unsaturated C_{14}, C_{16}, C_{20} *or* C_{22}.

Thus 86 per cent. of the whale oil glycerides contained one unsaturated C_{18} acid group (mainly oleic), whilst two of these groups were present in a further 6 per cent. of the oil. About two-thirds of the oil consisted of glycerides containing one molecule of oleic (or other unsaturated C_{18}) acid with one saturated acid, and one of the other homologous unsaturated acids.

About half of the glycerides of the oil contained no acids with more than 18 carbon atoms in the molecule ; this is the least unsaturated part of the fat, in which oleopalmitohexadecenoin, oleomyristohexadecenoin, oleomyristopalmitin, and similar glycerides must be the chief components. In the rest of the whale oil, one or more groups of the (largely polyethenoid) C_{20} and C_{22} acids occur ; about one-third of the fat contained one of these groups, whilst two of them may have been present in about 8 per cent. of the oil. Whilst glycerides with three polyethenoid groups were unlikely to be present in this specimen of whale oil, tri-unsaturated glycerides (in which one or two acyl groups are oleic, hexadecenoic, or tetradecenoic) amounted together to nearly 20 per cent. of the whale oil.

This study thus fully confirmed the earlier findings of Suzuki [1] and of and of Hilditch and Terleski [4] that the mixed glycerides of whale oil form an extremely complex mixture.

A similar examination of an Icelandic herring oil was carried out by Bjarnason and Meara.[40] In this case the oil was first crystallised from acetone at the lowest temperature employed (—40°), and the insoluble portion recrystallised from acetone at —30°, and so on.

The resulting data are summarised in Table 79.

From the component acids of the five fractions A to E it is possible, as in the case of whale oil (discussed above), to conceive of a large number of combinations of mixed triglycerides in each group ; and thus, again, it is not feasible to give any precise statement for the component glycerides. However, as with the whale oil, the series of component acid data reveal consistent alterations from the more saturated to the less saturated fractions which, with other features, point to maximum complexity or " even distribution " of fatty acids in the triglycerides throughout the herring oil. By applying this principle to the component acid data of each fraction it therefore becomes possible to suggest the probable composition of the whole herring oil—at least in general terms.

Before proceeding to record Bjarnason and Meara's final conclusions on this point, attention should be drawn to some features of the component acids of the herring oil. Table 79 (I) shows that in herring oil (as remarked earlier by Lovern [41]) no acid occurs in outstanding proportions. The three

TABLE 79. *COMPONENT ACIDS OF ICELANDIC HERRING OIL AND OF FRACTIONS SEPARATED BY LOW-TEMPERATURE CRYSTALLISATION (MOL. PER CENT.)*

	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
I. *Whole fat*						
Saturated	8·8	13·0	0·9	0·1	—	—
Unsaturated	1·5	13·3	20·0	24·0	18·3	0·1
Mean unsaturation	−2·0	−2·4	−3·5	−5·2	−4·3	−3·8
II. *Fractions separated by crystallisation*						
A. *Insoluble at* 0° (13·7 per cent.)						
Saturated	14·9	24·4	2·6	0·5	—	—
Unsaturated	0·9	4·9	12·4	15·5	23·9	—
Mean unsaturation	−2·0	−2·0	−2·3	−2·6	−2·5	—
B. *Soluble at* 0°, *insoluble at* −10° (19·7 per cent.)						
Saturated	12·1	17·2	1·5	0·1	—	—
Unsaturated	1·5	10·3	16·1	21·2	20·0	—
Mean unsaturation	−2·0	−2·0	−2·7	−3·1	−2·9	—
C. *Soluble at* −10°, *insoluble at* −30° (17·4 per cent.)						
Saturated	8·1	14·5	1·0	—	—	—
Unsaturated	1·3	12·9	20·5	25·2	16·5	—
Mean unsaturation	−2·0	−2·4	−3·1	−5·1	−3·5	—
D. *Soluble at* −30°, *insoluble at* −40° (19·0 per cent.)						
Saturated	7·6	10·9	—	—	—	—
Unsaturated	1·7	15·5	21·4	25·9	17·0	—
Mean unsaturation	−2·0	−2·3	−4·0	−5·9	−5·0	—
E. *Soluble at* −40° (30·2 per cent.)						
Saturated	5·3	5·6	—	—	—	—
Unsaturated	1·8	17·9	24·6	27·9	16·6	0·3
Mean unsaturation	−2·0	−2·6	−4·3	−7·2	−6·6	−3·8

groups of acids of the C_{18}, C_{20}, and C_{22} series respectively form 20, 24, and 18 per cent. of the total, with saturated and unsaturated C_{16} acids somewhat less (about 13 per cent. each), 9 per cent. of myristic acid, with about 1 per cent. each of stearic and tetradecenoic acids, and traces of lauric, arachidic, and tetracosenoic acids. There are moreover considerable, and curiously, approximately equal, proportions of mono-ethenoid acids in each homologous group of unsaturated acids. If the not unreasonable assumptions be made that the unsaturated acids are composed as follows :—

Unsaturated C_{16} mono-ethenoid and triethenoid
,, C_{18} ,, ,, tetra-ethenoid
,, C_{20} ,, ,, tetra-+penta-ethenoid
,, C_{22} ,, ,, penta-+hexa-ethenoid

it follows that the percentages in the total fatty acids of mono-ethenoid C_{16}, C_{18}, C_{20}, and C_{22} acids are respectively about 12, 15, 13, and 14 per cent. (mol.), those of the corresponding polyethenoid C_{16}, C_{18}, C_{20}, and C_{22} acids being about 1, 5, 11 and 5 per cent. (mol.) of the total fatty acids.

From consideration of all the above data Bjarnason and Meara concluded that the general glyceride composition of the Icelandic herring oil was most probably somewhat as follows :—

	Per Cent. Mol.
Tri-unsaturated (mixed mono-+polyethenoid glycerides)	35
Mono-saturated di-unsaturated (mono-+polyethenoid)	33
,, (mainly mono-ethenoid)	28
Disaturated mono-unsaturated (mainly mono-ethenoid)	4

Thus about one-third of the herring oil was made up of tri-unsaturated glycerides, nearly all of which may have contained both mono- and polyethenoid acids (including members of each homologous series). Apart from the small proportion of disaturated glycerides (probably myristo-palmito derivatives), the rest of the oil was nearly equally divided between monosaturated glycerides in which both a mono-ethenoid and polyethenoid acyl group was also present, and those in which both unsaturated groups belonged to homologous members of the mono-ethenoid series. In contrast to whale oil, about 40 per cent. (mol.) of the glycerides contained no unsaturated acid of the C_{18} series, whilst nearly all the triglycerides appeared to contain at least one C_{20} or C_{22} acyl group although none appeared to contain three.

The herring oil studied, containing five major component acids (four being unsaturated), exhibits an extremely complex mixture of mixed triglycerides, and offers further evidence of the general even distribution of fatty acids amongst the glycerol molecules of a marine animal oil.

A less extended study of menhaden oil (*Brevoortia tyrannus*) by Baldwin and Parks [42] serves to give partial corroboration of this extremely mixed glyceride structure in oils from the herring family. These workers found that about 12·5 per cent. of the oil, with an iodine value of 92·9, was insoluble in acetone at $-15°$, whilst a further 75 per cent. (iodine value 179·0) separated from acetone at $-60°$, leaving in solution at $-60°$ a residual 12·5 per cent., with an iodine value of 264·2. A very small portion of the original menhaden oil, separated on long standing at 15°, had iodine value 5·9, and contained chiefly myristic, palmitic, and stearic acids. Baldwin and Parks also adduced evidence indicating the presence of Δ^{9}- and of Δ^{10}-octadecenoic acids, with an octadecatetraenoic, Δ^{11}-eicosenoic, and an eicosapentaenoic acid in this oil.

The data discussed above refer to various fish and whale oils which are composed entirely of glycerides of the ordinary range of " aquatic " fatty acids. A few observations have been made with reference to the components of sperm whale oils (a mixture of glycerides and wax esters with the latter predominating) and of porpoise body fats, which contain the unusual *iso*valeric acid as a component, and are mainly glycerides with a very small proportion of wax esters.

Sperm whale oils. The head and blubber oils of the sperm whale, the unusual acid and alcohol components of which have already received notice (Chapter II, pp. 57–59), have been examined by Hilditch and Lovern [5] by means of the oxidation method; it was found that in both oils the fatty acids are united in the usual heterogeneous and complex manner both with glycerol and with the higher alcohols. The head oil contains about 26 per cent. and the blubber oil about 34 per cent. of glycerides, the rest in each case being wax esters of the higher alcohols.

Sperm head oil. Semi-quantitative examination of the saturated portions of the head oil revealed that in 100 parts of the original oil there were present about 3 parts of fully saturated glycerides, together with about 26 parts of wax esters built up entirely from saturated alcohols and acids; there was a marked tendency for the fatty acids of lower molecular weight (capric, lauric) to associate predominantly with the three saturated alcohols (tetradecyl, octadecyl, and cetyl, the last in much greater proportion than the first two). Further, about 24 parts of the oil were composed of esters of saturated acids with unsaturated alcohols, and about 18 parts of esters of unsaturated acids with saturated alcohols; the remainder of the oil (about 29 parts) consisted of esters of unsaturated acids and alcohols and of mixed saturated-unsaturated glycerides. There can be no marked proportion of cetyl palmitate present, since although cetyl alcohol is the major alcoholic component of the wax, palmitic acid is combined with it to a far less degree than lauric, myristic, and capric acids; the chief saturated wax esters present are undoubtedly cetyl laurate and myristate.

Sperm blubber oil. Although the blubber oil was not amenable to similar detailed treatment, the data obtained indicated that its general structure is not dissimilar from that of the head oil, and that it is a heterogeneous mixture of various wax esters (mainly liquid, owing to the more unsaturated character of both the alcohols and the acids present) and mixed triglycerides. Since oleyl alcohol is the chief alcoholic component, and oleic and hexadecenoic acids comprise the greater part of the fatty acids present, it is clear that both oleyl oleate and hexadecenoate are present in abundance

Porpoise body fat. Lovern [6] observed that the body fat (almost wholly glycerides) of a porpoise contained 10·5 per cent. by weight (12·9 per cent. mol.) of fully saturated glycerides. The molar percentages of the acids present in the whole fat and in the fully saturated glycerides were as follows:

	In Whole Fat Per Cent. (Mol.)	In Fully Saturated Part Per Cent. (Mol.)
Saturated:		
*Iso*valeric	28·7	43·6
Lauric	3·8	16·8
Myristic	11·4	31·5
Palmitic	3·9	8·1
Unsaturated:		
C_{14}	4·5 (−2·0H)	—
C_{16}	23·0 (−2·0H)	—
C_{18}	12·8 (−2·8H)	—
C_{20}	7·4 (−4·8H)	—
C_{22}	4·5 (−4·9H)	—

The glyceride structure of this fat appears somewhat curious in several respects. There is sufficient unsaturated acid present to produce a complete mixture of mixed saturated-unsaturated glycerides, but in fact about 13 mols. of triglycerides out of every 100 are fully saturated. In this respect, however, porpoise body oil falls in line with sperm head oil and with the depot fat of the amphibian green turtle [7]; both of these fats are also notable for the presence of unusual proportions of low molecular weight acids (*n*-decanoic, lauric, myristic).

The proportion of each of the total saturated fatty acids of porpoise body fat present in the form of fully saturated glycerides is *iso*valeric 20, lauric 60, myristic 36, and palmitic 27 per cent. This is in accordance with the corresponding features of sperm head oil in that larger proportions of the acids of lower molecular weight are combined as fully saturated material, except that the *iso*valeric acid is an outstanding exception. Only 20 per cent. of it is so combined, the remaining 80 per cent. being combined in glycerides which also contain at least one unsaturated acyl group. Whilst this is perhaps surprising, it nevertheless demonstrates very definitely that the abnormal *iso*valeric acid is interwoven with the more usual higher fatty acids into mixed glycerides of the customary type.

Depot fat of the Indian land crab. The crustacean *Birgus latro* (the Seychelles or Indian land crab) deposits a somewhat large proportion of fat in its tissues. The fat from specimens taken in the Seychelles Islands was examined by Hilditch and Murti,[43] and found to have a marked resemblance, in its general composition and its content of fully saturated glycerides, to coconut oil. The component acids of the whole fat, and of the 66·3 per cent. (mol.) of fully saturated glycerides which it contained, were as follows :—

Acid	Whole Fat Per Cent. (Mol.)	Fully Saturated Part Per Cent. (Mol.)
Octanoic	1·5	3·2
Decanoic	5·3	7·1
Lauric	47·5	54·8
Myristic	19·0	20·5
Palmitic	13·1	12·7
Stearic	1·7	1·7
Unsaturated C_{14}	0·7	—
,, C_{16}	2·2	—
,, C_{18}	6·8	—
,, C_{20-22}	2·2	—

Birgus latro, which is common on the shores of islands in the Indian Ocean from Zanzibar to the East Indies, is well known to make fallen coconuts its chief food, and it would appear that its fat is one of the instances in which the fat depots are supplied largely by assimilation from the diet, rather than by synthesis in the animal. The lauric and myristic acid contents of the land crab fat are very similar to those of coconut oil (Chapter IV, Table 59B, p. 202), and the lesser proportions of decanoic and, especially, of octanoic acid in the land crab fat further support the view that the main source of this depot fat is assimilated coconut fat, since it has been generally found that, when a fat containing glycerides of acids with less than 12 carbon atoms in the molecule is ingested by an animal, these lower fatty acids are not stored to any extent in the fat depots.

From the fully saturated glyceride content, it might be concluded that about 80 per cent. of the land crab fat was substantially derived from coconut fat ; if this were so, the remaining 20 per cent. would have been composed of glycerides of saturated (myristic and palmitic), unsaturated C_{16}, unsaturated C_{18}, and unsaturated C_{20-22} acids in the respective proportions of about 30, 15, 35, and 15 per cent., and would thus be broadly similar to those of some amphibious animals (*cf.* Chapter III, p. 69), and also to those of some types of marine animal fat.

Green turtle depot fat. The fat of the amphibian *Chelone mydas* may be included here, since its glyceride structure appears from the work of Green and Hilditch[7] to be more akin to those of the marine animals just dealt with than to that of land animals. The component acids of the original fat were *n*-decanoic 0·3, lauric 16·9, myristic 11·9, palmitic 17·0, stearic 3·7 ; unsaturated C_{14} 1·5, C_{16} 7·8 (−2·0H), C_{18} 35·8 (−2·2H), and C_{20} 5·1 (−6·3H) per cent. (mol.). Examination of fractions of the fat obtained by the acetone-crystallisation procedure (Chapter VI, p. 241) showed the presence of 9·6 per cent. (mol.) of fully saturated glycerides and about 9 per cent. (mol.) of tri-C_{18} glycerides. The acids in the fully saturated components were in the same proportions as those in which they occurred in the whole fat, and consisted of mixed glycerides of lauric, myristic, palmitic, and a little stearic acid. There is sufficient unsaturated acid (50 per cent. mol.)

to permit the turtle fat to be made up wholly of mixed saturated-unsaturated glycerides, whilst little more than a third of its acids are of the unsaturated C_{18} series ; yet it contains nearly 10 per cent. (mol.) each of fully saturated and of tri-C_{18} glycerides. The remaining 80 per cent. of the fat, on the other hand, contains a mixture of acids in very similar proportions to those in the whole of the fat.

The food of the green turtle is mainly herbivorous but they sometimes eat shell-fish, including young crabs. Since the specimen whose fat was examined came from the Seychelles Islands, it is possible, but perhaps not very likely, that its fat owes some of its peculiar composition to assimilation of land crab fat (*cf.* preceding paragraph) but this is of course no more than a speculation.

LAND ANIMAL DEPOT AND MILK FATS

The quantitative studies of the glyceride structure of land animal fats, as of vegetable seed and fruit-coat fats, rest primarily upon observations o the amount and nature of the fully saturated components which occur therein. It is therefore desirable to present a summary of these in tabular and graphical form (Table 80 and Fig. 3), similar to that employed for the vegetable fats (Chapter VI, Table 62 and Fig. 2). In the case of the animal

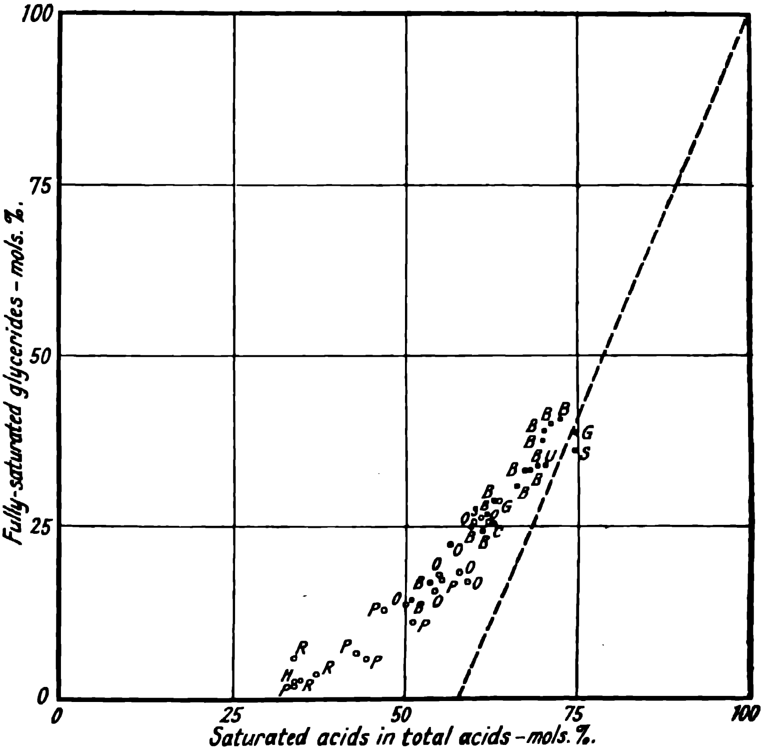

FIG. 3.

TABLE 80

FIG. 3		DEPOT FATS	SATURATED ACIDS IN TOTAL FATTY ACIDS			TOTAL	FULLY SATURATED GLYCERIDES PER CENT. (MOL.)
			MYRISTIC	PALMITIC	STEARIC	PER CENT. (MOL.)	
H	*Birds*	Domestic fowl (hen)	0·1	27·1	6·8	34·0	2·5
R	*Rodents*	Wild rabbit	5·4	24·5	3·8	33·7	6·0
R		Rat (low fat diet)	6·0	25·5	3·0	34·5	2·5
R		„ „ „	5·4	29·7	1·9	37·0	3·5
	Herbivora						
P	*Pigs*	Sow, outer back fat	4·6	21·7	7·6	33·9	2·2
P		„ inner „ „	2·8	27·3	14·4	44·5	5·6
P		„ „ „ „	4·6	27·7	10·6	42·9	6·7
P		„ perinephric fat	4·7	29·4	16·9	51·0	11·4
P		Hog, „ „	2·0	27·4	17·5	46·9	13·2
P		„ „ „	4·4	30·2	20·5	55·1	17·7
O	*Oxen*	Beef tallow, North American	7·5	29·1	13·4	50·0	13·9
O		Shorthorn bullock, perinephric fat	3·9	26·5	23·8*	54·2	15·8
O		„ heifer, „ „	2·7	33·4	22·7*	58·8	17·4
O		„ cow, „ „	3·5	31·0	20·4*	54·9	18·4
O		„ heifer, „ „	2·5	28·7	26·5*	57·7	18·6
O		Beef tallow, South American	5·3	32·9	18·2	56·4	22·8
O		„ „ „ „	9·5	29·2	23·2	61·9	25·8
O		„ „ „ „	6·9	25·5	27·4	59·8	26·0
M	*Sheep*	Mutton tallow	5·5	26·2	29·3	61·0	26·6
G	*Goat*		7·2†	27·0	28·9*	63·1	29·2
	Buffalo	Indian	3·9	33·4	32·2*	69·5	32·5
		„	8·8‡	45·6	19·5*	73·9	37·2

		MILK FATS	C_4-C_{14}	PALMITIC	STEARIC		
	Herbivora						
B	*Cows*	English, stall-fed, 1934 (cod liver oil in diet)	21·7	22·4	6·5*	50·6	14·6
B		„ „ „ „ „ „	22·9	22·8	7·8*	53·5	17·2
B		„ „ „ (linseed oil in diet)	32·7	20·0	8·6*	61·3	24·8
B		„ „ „ (rape oil in diet)	30·3	17·0	12·1*	59·4	25·3
B		„ spring pasture, 1929	32·2	24·3	5·4	61·9	27·2
B		„ autumn fed, 1928	28·8	27·1	7·1*	63·0	29·1
B		New Zealand, market sample, 1927	32·0	26·2	7·9*	66·1	31·5
B		Indian, pasture fed, 1930	35·6	26·8	5·5	67·9	33·7
B		New Zealand, market sample, 1927	30·9	25·7	10·7*	67·3	33·8
B		English, stall-fed, 1934	33·1	25·2	10·8*	69·1	34·2
B		„ „ 1929 (soya bean cake in diet)	38·7	23·7	7·6*	70·0	38·2
B		New Zealand, spring pasture, 1928	35·2	25·0	10·0*	70·2	39·6
B		English, stall-fed, 1934	40·3	20·5	10·6*	71·4	40·4
B		„ „ 1929 (coconut cake in diet)	44·4	24·1	3·9	72·4	41·3
U	*Buffalo*	Indian, pasture-fed, 1930	31·4	28·7	10·0*	70·1	34·3
		„ mainly pasture-fed, 1945	30·4	31·9	12·6*	74·9	41·7
		„ heavy cottonseed feed, 1945	17·7	25·1	20·1*	62·9	24·3
S	*Sheep*	Indian, winter diet, 1932	47·5	20·4	6·7*	74·6	36·8
G	*Goat*	Indian, winter diet, 1932	45·7	21·5	7·4*	74·6	39·3
C	*Camel*	Indian, pasture, 1933	24·6	28·3	9·7	62·6	25·6
	Omnivora						
	Human	English, 1944	18·8	23·6	7·4	49·8	9·1

* Including small amounts (up to about 1 per cent.) of arachidic acid.
† Includes 4·7 per cent. lauric acid.
‡ Includes 1·4 per cent. lauric acid.

fats, however, it will be well to give, in addition to the total percentage of saturated acids in the component acids of each fat, separate figures for the proportions of palmitic and stearic acids, and of acids of lower molecular weight than palmitic. Also, since in the milk fats the range of molecular weight of the saturated acids is very wide, it is desirable to give all quantitative data in this chapter in the form of molar proportions.

Fig. 3 should be compared with Fig. 2 in Chapter VI (p. 235) showing similar data for vegetable seed and fruit-coat fats. In Fig. 3 the purely " evenly distributed " types of mixed glycerides which are almost universally the rule in seed fats would fall on the horizontal axis as far as about 58 per cent. of saturated acids in the total fatty acids of a fat, and would thereafter follow the broken line inserted on the graph. It is clear that only those animal depot fats containing less than about 35 per cent. of saturated acids in the total fatty acids conform with this generalisation ; with increasing contents of saturated acids the proportions of fully saturated glycerides increase steadily, whether in depot or milk fats, and the relationship between content of fully saturated glycerides and of total saturated acids is obviously fundamentally different from that encountered in nearly all the vegetable fats (Chapter VI).

At the time (1930–1931) that this characteristic difference between the glyceride structures of certain classes of animal fats and many other fats (notably vegetable seed fats) became clear, it was noticed (Bhattacharya and Hilditch,[8] Banks and Hilditch [9a, 9b]) that the proportions of fully saturated glycerides in those animal fats which had been examined and which contained over 35 per cent. of saturated acids in their total fatty acids were not very different from that calculated on the basis of " random " or " indiscriminate " rather than " even " distribution. The mathematical probability of the percentage (y) of glycerides containing three saturated acyl groups being produced from a mixture of fatty acids containing x per cent. of saturated acids is determinable, since y will be proportional to x^3. In tallows, lards, and milk fats containing between 40 and 60 per cent. of saturated acids in the total fatty acids, it was seen [8a, 9b, 11b] that the observed proportions of fully saturated glycerides were slightly greater than that demanded by the relation $y \propto x^3$, although broadly speaking the curves expressing the relationship between fully saturated glyceride content and proportion of saturated acids in the total fatty acids were not dissimilar. It was also shown [8] that, when triglycerides or glycol di-esters were synthesised from a mixture of saturated and unsaturated acids in the laboratory by heating the mixed acids with glycerol or ethylene glycol in a vacuum at high temperatures (140–150°), the proportion of fully saturated triglycerides or of glycol esters with two saturated acyl groups also resembled, but was not identical with that calculated from the relations $y \propto x^3$ (triglycerides) or $y \propto x^2$ (glycol di-esters) With fatty acid mixtures containing less than 50 per cent. of saturated acids the amount of fully saturated esters produced was consistently slightly above that calculated on the probability basis, whilst with fatty acid mixtures containing over 50 per cent. of saturated acids the fully saturated ester content fell somewhat below the calculated figure.

The circumstance that some approximation to " indiscriminate " distribution of the saturated acids was apparent in the glycerides of animal depot milk fats with more than about 35 per cent. of saturated acids in their total fatty acids did not, however, commend itself as an adequate reason for assuming that, in these fats, so fundamentally different a mode of assemblage of triglycerides takes place from that which occurs in wide ranges of other natural fats, both vegetable and animal. It appeared indeed somewhat illogical to postulate profound constitutive differences of this character in different groups of natural fats, the elaboration of which is presumably due to the same, or broadly similar, conditions of enzyme systems, temperature, and so on. Moreover, it soon became clear that this apparent similarity to results based on " probability " considerations only held for the *saturated* acids. When similar consideration was given to the oleic acid content of this group of fats, it became increasingly evident that their content of triolein was small or even non-existent. The maximum reported figure so far is 3 per cent. of triolein, whereas, if the amount of this triglyceride were proportional to the cube of the percentage of oleic acid in the total fatty acids, fats whose mixed acids contained 40, 50, or 60 per cent. (for instance) of oleic acid should contain respectively about 6·5, 12·5, and 21·5 per cent. of triolein.

Therefore, although in 1941 Longenecker[10] was apparently inclined to revert to the simple view of " random " or " indiscriminate " distribution mentioned above, possible alternative explanations seem more likely. Indeed, it will be shown in the following paragraphs that the glyceride structure, both of depot fats and of milk fats with relatively high proportions of saturated acids, is consistent with the superposition of certain other chemical changes on an originally preformed mixture of palmitic and oleic acids (with minor amounts of other saturated and unsaturated acids) assembled on the lines of " even distribution " which are so characteristic of nearly all other classes of natural fats.

To elucidate further the distinctive differences of these groups of depot and milk fats from the rest of the natural fats, let us examine some of the numerical details included in Table 80. As already pointed out in Chapter I (p. 11), a most characteristic feature of all the land animal fats seems to be the presence, in something like constancy, of major proportions of palmitic acid—about 25–30 per cent. (mol.) of the total acids in depot fats, and somewhat less in milk fats. When the amounts of other saturated acids are relatively small in comparison with that of palmitic acid (as in the hen, rat, and pig (outer back) fats), the proportion of fully saturated components is insignificant and such fats are quite similar in this respect to, for instance, vegetable fats with similar mixtures of saturated and unsaturated component acids.

The divergence from the vegetable fats is only noticeable in the depot fats of pigs, oxen, etc., and in the milk fats of the cow and other herbivorous mammals. Inspection of the data for these *depot* fats in Table 80 shows that, in this group, the fully saturated glyceride content may rise to over 25 per cent. of the fat, the saturated acids meanwhile approaching 60 per cent. or more of the total acids ; but, in the saturated acids, it will be seen that the proportions of palmitic, and also of myristic (or lower) acids, remain of the same order throughout the series. The increase in saturated acid content is practically entirely due to increase in *stearic acid*. Indeed, these animal depot fats with more than 35 per cent. of saturated acids in the total fatty acids may be conveniently termed " *stearic-rich* " *animal depot fats*. There is, however, no *prima facie* reason why this increased proportion of stearic acid should result in such relatively high contents of fully saturated components. Indeed, curiously enough, the component acids of cacao butter are strikingly similar in their proportions to those of the mutton tallow in Table 80, yet cacao butter, like many other seed fats of similar saturated and unsaturated acid contents (*cf.* Chapter VI, Table 63, p. 236) contains negligible quantities of fully saturated glycerides. If, however, the precursors of these relatively saturated animal depot fats were mixed glycerides of palmitic and oleic acids, and these had subsequently undergone, as *glycerides*, a partial saturation process, the observed relationships are exactly those which would be expected. The writer and his colleagues[9a, 9b, 9c] therefore put forward the hypothesis that, in the animal depot fats under discussion, the final mixture of component glycerides is the consequence of a bio-hydrogenation process which has operated *after* the precursor fatty acids (mainly palmitic and oleic) have been assembled into triglycerides according to what seems to be the general rule of mixed glyceride or " evenly distributed " glyceride production.

The graphical data for this group of depot fats and for the milk fats are shown on an enlarged scale in Fig. 4. The entire range of points obtained, when fully saturated glyceride content is plotted against total saturated acid content of the fats, are clustered round a smooth curve which intersects the horizontal axis at a point corresponding to 25–30 per cent. of saturated acids—the amount of palmitic acid invariably found in these fats. The abnormal increase in fully saturated glycerides in the depot fats runs exactly parallel with increasing amounts of stearic acid present in the glycerides. The observed relationships can, in fact, readily be explained by the hypothesis that, in these depot fats, the increased proportions of fully saturated glycerides are due to hydrogenation or saturation of pre-formed oleo-glycerides into stearo-glycerides. This possibility is well illustrated by the curve (Fig. 4) obtained when a pig depot fat of low stearic acid content was hydrogenated under laboratory conditions.[9c]

It will be seen, however, that the relationships for *milk fats* fall in exactly the same category as those for *depot fats* ; indeed the two series of fats overlap on the graph, the most unsaturated butter fats containing a smaller proportion of saturated acids than the most saturated tallows.

If we again consult Table 80, it will be seen that, in the *milk fat* component saturated acids, there is again a tendency to a constant proportion of palmitic acid (although the average molar proportion of the latter is probably somewhat below rather than above 25 per cent. in the milk fats, as compared with 25–30 per cent. in the depot fats). The increase in total saturated acids, which in many instances is more marked than in the depot fats (the saturated acids sometimes forming 70 per cent. or more of the total acids), is here however not due to any great extent to the presence of *stearic acid.* The *stearic acid* content of milk fatty acids is never very large, and the normal figure of 8–10 per cent. does not represent a very great increase over that of relatively unsaturated depot fats such as pig outer back fat or hen fats. The great increase in saturated acids in the milk fats is due, of course, to the very marked presence of *saturated acids of lower molecular weight* (butyric acid upwards).

Achaya and Banerjee[48a] have noticed (1946) that depot and milk fats of Indian ox and buffalo tend to contain about 3–4 units per cent. more of palmitic acid than those of cattle grown in the cooler European climates, the respective average proportions being about 33 and 30 per cent. for depot fats (*cf.* Chapter III, p. 91), and about 27 and 24–25 per cent. for the milk fats. Further, they show that, when plotted against the total proportion of saturated acids in each fat (as in Fig. 4), the fully saturated glyceride content of seven milk fats and four depot fats from different Indian animals lie on an almost smooth curve which, when projected, cuts the horizontal axis at a point corresponding to about 35 per cent. of saturated acids; whereas (as stated above) the curve for corresponding European depot and milk fats intersects the horizontal axis at about 30 per cent. of saturated acids. This observation appears to point still more clearly to a significant connection between the fully saturated glyceride contents and the palmitic acid contents of the respective fats.

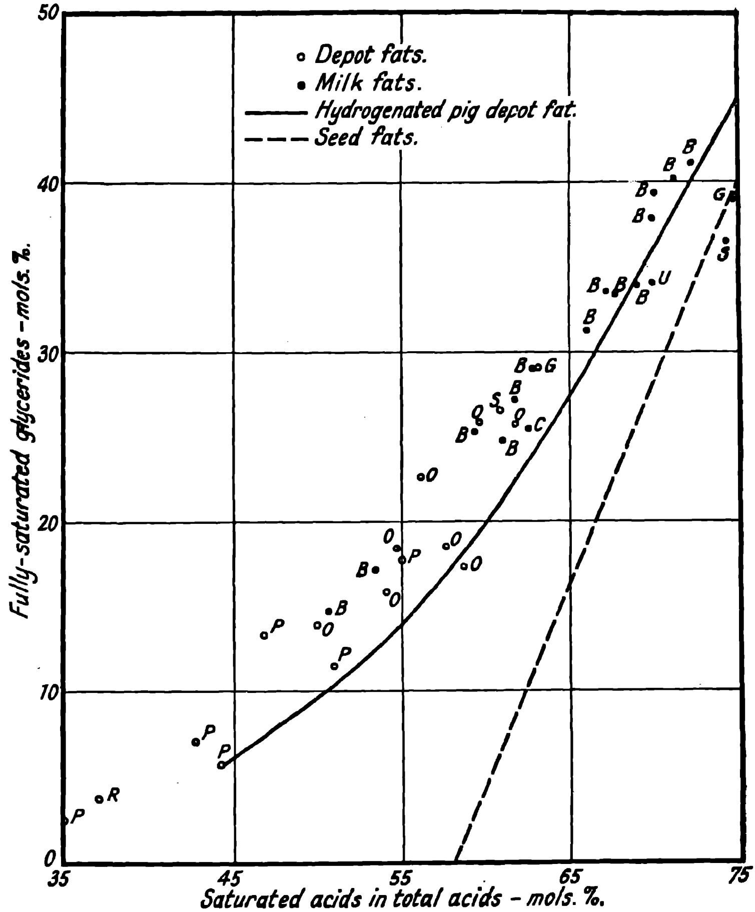

FIG. 4.

The general relationships shown in Fig. 4 are explicable, in the milk fats as in the depot fats, if it can be supposed that in both groups saturated glycerides have resulted from transformation of pre-formed *oleo-glycerides*; but, of course, to apply this hypothesis to the milk fat glycerides involves much more than the simple hydrogenation of oleo-glycerides. It demands the conversion of an oleo-glyceride into, for example, a butyro- or capro-glyceride, and this in turn involves a process of combined oxidation and reduction in which, moreover, a free carboxyl group must not be concerned, since it is the glyceride itself which must be transformed. This conception seems less unlikely at the present time than when it was first suggested by Hilditch and Sleightholme [11] in 1930. At that time it was generally held that blood phospholipids were the probable precursors of milk fat, but subsequently, and especially in consequence of the work of Graham, Jones, and Kay,[12] of Maynard, McCay *et al.*,[13] and of Shaw and Petersen,[14] it has been shown that milk fat glycerides are derived mainly from the non-phospholipid fatty acids of blood, probably from those of neutral fat (glycerides).* Moreover, the former view that oxidation of fats *in vivo* was confined to the "β"-oxidation process commencing from the free carboxylic acid groups has been modified and extended by Jowett and Quastel's [15] conception of "multiple alternate oxidation," i.e. oxidation at alternate carbon atoms of a long carbon chain; while Verkade and Lee [16] have shown that, under certain conditions, oxidation of a terminal methyl group takes place in the living organism. *Prima facie*, therefore, the hypothesis that lower saturated fatty glycerides might be produced *in vivo* from preformed oleo-glycerides is not in fundamental conflict with the present views on the precursors of milk fat, or on the mechanism of oxidation processes possible in a long carbon chain.

There is at present no definite proof of the correctness of these hypotheses. Indirect evidence of various kinds seems however to afford considerable support for them, and may be summed up as follows for each of the two groups—depot and milk fats:

DEPOT FATS

(*a*) Abnormal increase in fully saturated glyceride content only commences when stearic acid is present in more than minor proportions, and then runs exactly parallel with the increasing amounts of stearic acid present in the depot fat.

(*b*) The relationship between fully saturated glyceride and total saturated acid contents when a pig fat (of the more unsaturated type) is progressively hydrogenated to varying extents follows the same course as that shown by the series of natural depot fats of increasing saturation; the glyceride structure of the pig fat after hydrogenation to states corresponding with some of the ox or sheep depot fats was similar to that of the latter (Hilditch and Stainsby).[9c]

* Graham *et al.*[17], finding (1938) that the respiratory quotient of the metabolic processes in the mammary gland is considerably above unity, concluded that glycerides are being synthesised therein from carbohydrates. Shaw and Peterson [14] (1940), however, found that the uptake of glucose and amino-acids in the gland was not material, and subscribed to the view that most, if not all, of the milk fat is derived from blood fat. They suggest that some other explanation must be sought for the high respiratory quotient reported by Graham *et al.*, and consider that the evident (inverse) relationship between the oleic acid and the short chain acids is due to a breakdown of oleic glycerides as suggested above.

(c) The most conclusive, although of course still "circumstantial," evidence for the view that a preformed mixture of "evenly distributed" oleo-glycerides has undergone partial bio-hydrogenation to stearo-glycerides prior to its appearance as animal depot fat is to be found, however, in the more detailed accounts of the component glycerides present in a group of depot fats of widely varying mean unsaturation which have resulted from the use of the preliminary acetone-crystallisation process described in Chapter VI (pp. 241, 242). This was first applied to an English ox depot fat by Hilditch and Paul,[18a] and subsequently to two Indian cow depot fats,[18b] and to the external and perinephric tissue fats of a pig [19] and a sheep.[20] Fuller details of these data are quoted later in this chapter (pp. 317–320), from which it will be seen that the proportions in these seven fats of (i) triolein, stearodiolein, oleodistearin, and tristearin, (ii) palmitodiolein, oleopalmitostearin, and palmitodistearin, and (iii) oleodipalmitin and dipalmitostearin, considered in relation to the oleic and stearic acid contents of each fat, follow exactly the sequence which would be expected if part of the oleo-glycerides had been converted into stearo-glycerides by saturation with hydrogen atoms, this process being considered as one of "indiscriminate" selection of the double bonds which may undergo or escape hydrogenation.

Furthermore, attempts to reproduce the observed glyceride composition by arithmetical distribution of the oleic acid content amongst the palmitic and stearic acids of the fats (*cf.* Chapter VI, pp. 249, 250) led to an interesting observation. Inevitably, application of this method of "computation" to the total fatty acids of each depot fat leads in these cases to figures (p. 324) which bear no relation to those actually determined by the component glyceride analyses. If, however, the amounts of palmitic and stearic acids present in the fully saturated glycerides were first deducted from those in the whole fat, and the oleic acid arithmetically proportioned between the residual palmitic and stearic acids (i.e. that present in the mixed saturated-unsaturated glycerides of the fat), the proportions of palmito- and stearo-dioleins, oleopalmitostearin, etc., so "computed" reproduced (extremely closely in most instances) the figures obtained experimentally. This appears to give further support, perhaps of a somewhat striking character, to the general explanation outlined above.

Finally, it may be pointed out that the preformed oleo-glycerides, which, on the above hypothesis, have in the first place resulted by "even distribution," are postulated to originate from a mixture of fatty acids in which about 30 per cent. of palmitic acid is the main saturated portion; consequently (*cf.* Chapter VI, p. 237) their glyceride structure would be little different whether "even" or "random" distribution had operated at this stage. The superposing of partial addition of hydrogen—on a "random" basis—to the oleo-groups might therefore be expected to give proportions of palmitostearins which, so far as these fully saturated components were concerned, would not be very dissimilar from those derived by calculation on probability considerations from the proportions of saturated acids observed in the total fatty acids. This probably accounts for the resemblance to "random" distribution in the proportions of fully saturated glycerides in these fats as a whole, observed in the early days of quantitative study of glyceride structure by Hilditch and co-workers,[8, 9] and more recently by Longenecker.[10]

MILK FATS

(*a*) Glycerides present in the blood stream of the cow are the precursors of milk fats.[12, 13, 14]

(*b*) Bio-oxidation of long acyl chains by mechanisms other than β-oxidation from the carboxyl group of a free fatty acid is now known to take place in certain conditions.[15, 16]

(*c*) In milk fats, minor amounts of lower unsaturated acids are present, from Δ^9-decenoic acid upwards, in all of which the ethylenic linking is situated in the same position (with respect to the carboxyl group) as in oleic acid. The molar percentages of these acids present in the total acids of a typical cow milk fat were found by Hilditch and Longenecker [21] to be as follows:

		PER CENT. (MOL.)
OLEIC ACID	$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.COOH$	24·8
Δ^9-Hexadecenoic	$CH_3.[CH_2]_5.CH{:}CH.[CH_2]_7.COOH$	3·7
Δ^9-Tetradecenoic	$CH_3.[CH_2]_3.CH{:}CH.[CH_2]_7.COOH$	1·7
Δ^9-Dodecenoic	$CH_3.CH_2.CH{:}CH.[CH_2]_7.COOH$	0·5
Δ^9-Decenoic	$CH_2{:}CH.[CH_2]_7.COOH$	0·4

The presence, in regularly decreasing amounts, of these Δ^9-monoethenoid acids of lower molecular size than oleic acid, together with the proved absence of any unsaturated acid lower in the series than decenoic acid, suggests that they may represent, so to speak, fragments of transformed oleo-glycerides which have escaped complete saturation to lower saturated glycerides. (If this be the case, the production in milk fat of, for instance, a butyro-glyceride is the result of successive removal of terminal $CH_3.CH_2$—groups from an oleo-glyceride and succeeding lower glycerides by an oxidation-reduction process, whilst that of a decano (capric)-glyceride would represent an intermediate stage in the process, coupled with saturation of the Δ^9-ethenoid bond originally present.)

If, as some recent observations may seem to suggest (*cf.* p. 310), linoleo-glycerides in the blood stream are also involved as precursors of milk fats, the almost complete absence of ordinary linoleic (*cis-cis*-$\Delta^{9,12}$-octadecadienoic) acid from cow and other milk fats would give the impression that their transformation to shorter chain glycerides is much more complete than that of oleo-glycerides. The formation of these shorter chain products (including the minor amounts of Δ^9-ethenoid acids from decenoic acid upwards) could of course be visualised from either oleic or linoleic acyl groups in the blood-glyceride molecules.

Further indirect evidence on the factors affecting the production of cow milk glycerides is available when the effects of feeding specific fatty oils to cows, or of certain conditions such as fasting or ketosis, are considered. If the characteristic components of the milk fat are due to the operation of a specific metabolic process in the milk glands upon the blood glycerides passing though it, disturbances of the system in question as the result of some of the conditions mentioned might interfere. Such evidence as is available, indeed, suggests that this in fact occurs.

(*d*) **Effect of specific fatty oils in the diet on the composition of cow milk fats.** When unsaturated seed oils, e.g. linseed or soya bean oils, are included in the diet of dairy cows the polyethenoid acids (linoleic and linolenic) of the seed fat do not pass to an appreciable extent into the milk fat, but on the other hand if a fish oil is added in the diet, its characteristic polyethenoid C_{20} and C_{22} acids appear in the milk fat in some quantity. In the former instances the composition of the milk fat is little altered; in the latter the amount of the short-chain component acids is markedly reduced.

When cod liver oil is included in the diet of cows there is, in addition to a lowered production of milk fat, a very marked alteration in its composition (Hilditch and Thompson).[22] The lower saturated fatty acids are reduced to about half their usual proportion, the myristic and stearic acid contents are also reduced, but to a less extent, while the oleic acid content is considerably increased, and several per cent. of the highly unsaturated C_{20} and C_{22} acids, characteristic of cod liver oil, appear instead of the usual fractional percentage of " arachidonic " acid (Table 81; see also Chapter III, Tables 43B and 44B).

TABLE 81. *COMPONENT ACIDS* OF MILK FATS FROM A COW RECEIVING COD LIVER OIL (WEIGHT PER CENT.)*

Acid	Normal Diet	With Cod Liver Oil
Butyric	4·4	2·1
Caproic	1·8	0·9
Caprylic	2·1	0·5
Capric	2·8	1·2
Lauric	3·8	3·1
Myristic	10·1	6·4
Palmitic	25·3	22·7
Stearic	12·4	6·7
as Arachidic	0·8	0·6
as Oleic	31·0	43·3
as Octadecadienoic	4·4	4·8
as C_{20-22} unsaturated	1·1	7·7

* Minor unsaturated acid components not included.

When linseed or rape oil is similarly fed, the corresponding milk fats are unaffected as regards the proportions of lower saturated acids present, the only significant alteration being an increased oleic acid content balanced by somewhat less palmitic and/or myristic and stearic acids. A little of the C_{22} mono-ethenoid erucic acid of rape oil appears in the milk fat, but on a linseed oil diet the characteristic linolenic and linoleic acids of this oil do not appear in detectable amounts in the milk fat.

The highly unsaturated C_{20} and C_{22} acids of cod liver oil, however, evidently pass into the milk glands to quite an appreciable extent. The effect on the yield and composition of the milk fat is of a temporary nature, i.e. the milk fat returns to normal within a few days after the cod liver oil diet is stopped. The effect is consistent with a temporary interference with the enzymes concerned in milk fat elaboration; if the formation of the lower fatty glycerides of butter is due to enzymic oxidation-reduction of oleo-glycerides, highly unsaturated glycerides of the cod liver oil will undoubtedly be preferentially adsorbed by the enzymes concerned, which would therefore be hindered from carrying out their normal functions.

If, instead of comparing the percentage compositions of the butter fatty acids, the latter are used (in conjunction with the weights of butter fat produced over a definite period) to obtain a rough measure of the weight of each component acid produced in this period as butter glycerides (Table 82), the effect on the total yield of milk fat is seen, together with the following points concerning individual acids: butyric and caproic acid production is reduced to one-third of the normal; that of butyric-lauric (taken together) is similarly reduced; myristic and stearic production is reduced by over 50 per cent., palmitic by about one-third, while the amount of oleo-glycerides produced is unaffected or very slightly reduced. In other words, the glycerides which suffer most in production are precisely those which, on the hypothesis suggested, are produced by oxidation-reduction processes from oleo-glycerides.

TABLE 82. *APPROXIMATE WEIGHT PRODUCTION OF MILK FATTY ACIDS IN A COW RECEIVING 4 OZ. DAILY OF COD LIVER OIL IN FOOD*

(Combined milk from 2 cows collected over 4-day periods in each case)

	BEFORE LB.	DURING LB.	IMMEDIATELY AFTER LB.	AFTER 2 WEEKS LB.
Milk fat production (2 cows) over 4-day period.	7·91	5·60	5·33	7·76
Corresponding butter fatty acids	7·51	5·33	5·07	7·37
Butyric acid	0·33	0·11	0·11	0·33
Caproic ,,	0·13	0·05	0·05	0·13
Caprylic ,,	0·16	0·03	0·03	0·16
Capric ,,	0·22	0·06	0·06	0·22
Lauric ,,	0·28	0·16	0·16	0·27
Myristic ,,	0·76	0·34	0·32	0·75
Palmitic ,,	1·90	1·21	1·15	1·86
Stearic ,.	0·93	0·36	0·34	0·91
Arachidic ,,	0·06	0·03	0·03	0·06
Oleic ,,	2·33	2·31	2·19	2·28
Octadecadienoic acid	0·33	0·26	0·24	0·32
$C_{20\text{-}22}$ unsaturated acids	0·08	0·41	0·39	0·08

(*e*) **Effect of fasting (inanition) on composition of milk fat.** Smith and Dastur[23a] observed in 1938 that when lactating cows are caused to fast for several days the yield of milk fat falls considerably whilst its component acids undergo marked alteration—qualitatively similar to that observed during ingestion of cod liver oil. These workers made detailed analyses of the milk fat acids which are reproduced in Table 83.

Whilst the proportion of higher saturated acids (palmitic and stearic) remained almost unaffected as a result of inanition, the sum of the molar percentages of all the lower acids up to and including C_{14} fell by 24·2 during inanition, this being almost compensated by an increase of about 20 in the molar percentage of oleic acid. The proportions of butyric and myristic acids were reduced by about two-thirds, and those of the intervening acids by about seven-eighths, but palmitic acid only declined by about 5 per cent., and the amount of stearic acid was increased from 9·8 to 83·5 per cent., or by almost 40 per cent. The authors discussed the significance of these results in the light of possible production of milk fat either from blood glycerides or by synthesis from carbohydrate in the mammary gland, and concluded that it was not possible to decide which of the various theories was correct. In their view the fact of chief importance emerging from their results was the inverse relationship existing between the oleic acid on the one hand and the lower acids on the other. Later, Smith[23b] has reviewed the evidence in favour of the view that the lower milk fatty acids result from transformation of oleo-glycerides in the mammary gland, drawing attention to certain points which still require to be reconciled with it, and pointing out that ultimate proof of its correctness is still required.

TABLE 83. *COMPONENT ACIDS OF COW MILK FAT BEFORE AND DURING INANITION*

Acid	Wt. per 100 g.			Molecules per 100 Molecules		
	Cow No. 1		Cow No. 2	Cow No. 1		Cow No. 2
	Before Inanition	During Inanition *	During Inanition †	Before Inanition	During Inanition *	During Inanition †
Saturated:						
C_4	3·5	1·2	2·7	9·7	3·5	7·9
C_6	0·6	—	0·1	1·2	—	0·1
C_8	1·0	0·1	0·1	1·6	0·2	0·2
C_{10}	1·8	0·2	1·0	2·5	0·3	1·5
C_{12}	2·5	0·1	0·6	3·0	0·2	0·7
C_{14}	11·9	2·8	3·8	12·5	3·2	4·3
C_{16}	23·5	20·0	22·1	22·1	20·9	22·1
C_{18}	11·6	14·3	9·9	9·8	13·5	8·9
C_{20}	1·1	0·9	0·9	0·8	0·8	0·8
Total	57·5	39·6	41·2	63·2	42·6	46·5
Unsaturated:						
C_{10}	0·2	—	0·2‡	0·3	—	0·2
C_{12}	0·2	—	0·2‡	0·3	—	0·3
C_{14}	0·9	0·4‡	0·4‡	1·0	0·5	0·5
C_{16}	3·2	1·4	2·0	3·0	1·5	2·0
Oleic	35·9	52·8	51·7	30·5	50·1	46·9
Linoleic	1·2	2·5	0·8	1·0	2·4	0·7
C_{20}	0·8	3·3	3·5	0·6	2·9	2·9
Total	42·4	60·4	58·8	36·7	57·4	53·5
Total of all the acids up to C_{14}	22·6	4·8	9·1	32·1	7·9	15·7

* A sample obtained by mixing the fat secreted on the 11th and 12th days of inanition.

† A pooled sample from the fat secreted on the last six days of inanition.

‡ Where the amount of lower acids present is very low and oleic acid predominates as in the fats of inanition, it is probable that the figures marked ‡ are somewhat higher than the true values.

(*f*) **Effect of ketosis on the composition of cow milk fats.** In 1941–1942 Shaw *et al.*[24] drew attention to the effect of ketosis on the component acids of cow milk fats, employing the indications afforded by saponification, Reichert-Meissl, Polenske, and iodine values as a guide, without recourse to detailed component acid analyses. Nevertheless they were able to show that in cases of severe ketosis the short chain fatty acids of the cow milk fats were considerably reduced whilst the oleic acid was augmented. On treatment by glucose therapy the cows recovered rapidly, and at the same time the component acids reverted to their normal composition. Shaw *et al.* pointed out that the lower acids of the milk fats are not diminished nearly as much by ketosis as by short periods of fasting, although the blood glucose is usually lowered by at least 50 per cent. more in severe ketosis than after a few days of inanition. Qualitatively, however, the alterations produced either by lack of food or by ketosis are similar, and consistent in both instances with less profound alteration than that which normally proceeds during the conversion of blood glycerides into milk fat.

It is evident that the results of these studies of physiological or pathological conditions of animals in relation to the composition of their milk fats have proved very fruitful and enlightening, and it is to be hoped that further work on these lines will be developed. Indeed, ultimate proof of the chemical processes involved can only be looked for from more definitely physiological investigations. Deduction of possible or probable metabolic changes from examination (intensive or less so) of their end products can never lead to rigorous justification of theoretical explanations which may be propounded. It is, in fact, likely that this method of approach has now been explored almost to the limits in which it can be of service as a guide to the possible metabolic processes involved; although further advances may well be made in the direction of still more precise statements of component glycerides by further development of the experimental methods of separation and analysis, and also in compiling more exact component glyceride data for fats (both milk and depot) covering a much wider range of animal species than has yet been investigated.

Another experimental field, admittedly difficult by reason of the large amounts of the original source which are requisite, but much needed in connection with the study of animal fats, is the full examination of the fatty acids in the various blood lipids, especially perhaps the blood glycerides. Only two communications, both referring to the blood lipids of the ox, have yet been made in which anything approaching a complete statement is forthcoming, and there is room for much more work of this character on the blood lipids of different species.

From one of the communications mentioned, and from the specific features of human milk fat and of mare milk fat, it may be hazarded that ordinary or seed fat linoleic acid may be a more prominent constituent of blood lipids, and of certain milk fats, than would appear from study of ox or sheep depot and milk fats alone. It may indeed prove later that linoleo-glycerides, rather than oleo-glycerides, are those which most readily undergo transformation into other forms; but, in the absence of very many more experimentally established facts, this is at present a more or less remote speculation.

The immediate need is for much more, and much wider, experimental data than for further hypotheses. Whatever may be the finally accepted explanation of the production of depot or milk fats, however, it may once more be insisted that any such explanation must account for the general structure of the individual mixed glycerides present, and especially for the very specific and characteristic relationships subsisting between the contents of fully saturated glycerides and the total unsaturation of the fats (Table 80, figs. 3 and 4)—a feature which is perhaps not yet quite adequately appreciated by workers in this field.

Component Glycerides of some Individual Animal Fats

DEPOT FATS

Bird and rodent depot fats. The glyceride structures of the depot fats of the rat and the rabbit have only been defined in so far as their relatively small contents of fully saturated components (mainly tripalmitin) are concerned (*cf.* Table 80, p. 298).

The abdominal and gizzard fats of *Light Sussex hens* have been studied in somewhat greater detail by Hilditch and Stainsby.[25] The component acids of the mixed fats included: myristic 0·1, palmitic 27·1, stearic 6·7, hexadecenoic 7·9, oleic 36·2, linoleic 21·5, and C_{20-22} unsaturated 0·5 per cent. (mol.). Fully saturated glycerides formed only 2·5 per cent. of the fat, their component acids being (approximately) palmitic 85, and stearic 15 per cent.; the fully saturated components were thus mainly tripalmitin with some palmitostearins.

When completely hydrogenated, the fat contained 28–29 per cent. of tristearin; the glycerides of the original fat had accordingly the following approximate molar composition: tri-C_{18} 28–29, mono-C_{16}-di-C_{18} 41, di-C_{16}-mono-C_{18} 28–29, and tripalmitin 2 per cent. A specimen of the hen fat which had been hydrogenated to an iodine value of 14·6 (i.e. to the stage when the ratio of saturated to unsaturated acyl groups was approximately 5 : 1) was also examined and found to contain 58·5 per cent. of fully saturated components, made up approximately as follows: tristearin 10, palmitodistearin 38, dipalmitostearin 8·5, and tripalmitin 2 per cent. The composition of the fully saturated part of this incompletely hydrogenated fat showed that di-C_{16} glycerides were still present in quantity in the mixed saturated-unsaturated glycerides present. This is unusual at this stage of the hydrogenation of a fat containing less than 30 per cent. of combined palmitic acid, and points to the presence in the original fat of considerable proportions of palmito-hexadeceno-" oleins." (The hexadecenoic acid content (8 per cent.) of the fat would suffice to give 24 per cent. of such glycerides, compared with the observed total content of 28–29 per cent. of di-C_{16} glycerides.)

Hilditch and Stainsby concluded that the probable components of the hen fat were somewhat as follows:

GENERAL TYPE		PER CENT. (MOL.)
Fully saturated	Mainly tripalmitin with small amounts of palmitostearins	2
Di-C_{16}-mono-C_{18} glycerides.	Probably largely palmito-hexadeceno-" oleins," but might include up to 20 per cent. of palmito-hexadeceno-stearins.	28–29
Monopalmitodi-C_{18} glycerides.	Palmitodi-" oleins " (but including up to 20 per cent. of " oleo "-palmitostearins).	41
Tri-C_{18} glycerides	Tri-unsaturated, probably oleo-linoleins (but might include up to 20 per cent. of stearodi-" oleins ").	28–29

The 7 per cent. of stearic acid combined in the fat could not be definitely allocated by the experimental methods employed in the case of this fat, but must be distributed in about 20 per cent. of the mixed glycerides of the whole fat, i.e. in some or all of the three groups indicated above.

Hen body fats are differentiated from the corresponding fats of pigs, sheep, cows, and some other animals (*vide infra*) by their unusually large proportions of tri-C_{18} (unsaturated) glycerides and, especially, of the mixed semi-unsaturated di-C_{16}-mono-C_{18} glycerides. The result is a more heterogeneous mixture of mixed triglycerides than in fats of the lard type. This is reflected in the physical consistency of the fats. A pig fat of similar mean unsaturation and not very different palmitic, stearic, oleic, and linoleic acid contents forms a thin, semi-solid, almost homogeneous paste at atmospheric temperature ; but the hen body fats separate into two well-marked phases —a clear liquid fat with a lower layer of solid glycerides (so-called " stearin ").

DEPOT FATS OF THE HERBIVORA

Studies of the glyceride structure of herbivorous animal depot fats have so far been almost wholly concerned with the " *stearic-rich* " group, i.e. with depot fats in which stearic acid forms from 10 per cent. up to nearly 30 per cent. of the total component acids. (No body fat from a wholly carnivorous animal, it may be remarked, has yet been examined with reference to its component glycerides.)

Ceylon bear and sacred baboon body fats. The depot fats of two animals whose food is predominantly vegetable in character, and which contain only small proportions of stearic acid, have however been studied [33] by the low-temperature acetone crystallisation procedure (Chapter VI, pp. 241–243 ; this Chapter, pp. 290–292). The bear fat (369 g.) was separated between 0° and –30° into five fractions of varying order of solubility, and the baboon fat (39 g.) into two fractions (at –10° C.), the component glycerides in each fraction being estimated from the composition of their component acids. The results are summed up in Table 84.

TABLE 84

(i) *Component Fatty Acids* (*Molar Percentages*)

	Ceylon Bear Per Cent.	Sacred Baboon Per Cent.
Lauric	0·5	—
Myristic	4·4	2·7
Palmitic	28·0	18·4
Stearic	2·4	7·6
Dodecenoic	0·4	—
Tetradecenoic	1·6	1·2
Hexadecenoic	11·8	6·8
Oleic	49·1	50·1
Octadecadienoic	1·1	12·5
Unsaturated C_{20-22}	0·7	0·7

(ii) *Probable Component Glycerides* (*approx. Molar Percentages*)

Dipalmitostearin	2	Trace
" Oleo "-dipalmitin	11	—
" Oleo "-palmitostearin	5	Some
Palmitohexadeceno-" olein "	21–28	15
Palmitodi-" olein "	47–40	40
Stearodi-" olein "	—	15
Dihexadeceno-mono-" olein "	7–nil	—
Hexadecenodi-" olein "	7–14	20
Linoleodi-" olein "	—	

The main component in each of these two fats is evidently palmitodiolein (this term here including myristic with palmitic, and linoleic with oleic, acids). Owing to the significant proportions of hexadecenoic acid, especially in the bear fat, important amounts of glycerides containing both hexadecenoic and " oleic " acids are in evidence. About 70 per cent. of each fat consists of di-unsaturated glycerides, and about 15–20 per cent. is mixed tri-unsaturated glycerides (in which hexadecenoic, or octadecadienoic, acid accompanies oleic acid).

The experimental data are fairly closely simulated arithmetically when the oleic acid is partitioned amongst the rest of the acids in the manner described in Chapter VI (pp. 249, 250). It is thus evident that the general rules of " even distribution " which govern the composition of vegetable fats are operative in these two animal fats, in which stearic acid is only a minor component.

" STEARIC-RICH " ANIMAL DEPOT FATS

This group has received much investigation, especially in the cases of pig, ox and sheep body fats. After many observations based on the content and composition of the fully saturated glycerides in these fats, or in their partly hydrogenated products, had been recorded, the more elaborate acetone crystallisation procedure was applied to a group of two ox, two sheep and two pig fats, the component acids of which formed a progressive series with increasing stearic and diminishing oleic acid content. This series, taken together, presents a rather complete picture of the progressive changes in glyceride structure consequent upon the alterations in the proportions of the two acids mentioned, and it is therefore preferable to discuss this group as a whole, rather than in terms of the various animals concerned.

Before dealing with these later observations, however, it will be well to review the main results of the earlier, less detailed, work which was carried out on the fully saturated glycerides present in the fats of the different animals or of their partly hydrogenated products.

STUDY OF FULLY SATURATED GLYCERIDES IN PIG, OX, SHEEP AND GOAT FATS

Pig depot fats. Partial quantitative studies of pig depot fats included examination of the proportions and composition of their fully saturated glycerides,[9b] and study of the products formed during progressive hydrogenation of a pig back fat.[9c] Banks and Hilditch[9b] studied five pig fats : the outer and the inner layers of the back fat and the perinephric or leaf fat from an individual sow, and two perinephric fats from members of the same litter which had been fed respectively on a fat-free diet and on the same diet with the addition of 3 per cent. of groundnut oil.[26] The data obtained in this series are summarised in Table 85.

From the " association ratios " of the saturated and unsaturated acids in the non-fully saturated components of these fats (Table 85 (ii), final column) the limits between which the respective proportions of mono-" oleo "-and di-" oleo "-glycerides and of tri-unsaturated glycerides must lie may be calculated ; the later, more detailed, work indicates, as a matter of fact, that the proportion of tri-unsaturated glycerides in pig fats is not large.

The component acids of the fully saturated glycerides (Table 85 (iii)) show more approach to constancy in composition than the saturated acids in the whole fats. Whilst the ratios of palmitic (plus the small amounts of myristic) to stearic acid in the whole fats lie between the extremes of about

TABLE 85. *PIG DEPOT FATS*

(i) *Component Fatty Acids of the Whole Fat (Molar Percentages)*

	Myristic Per Cent.	Palmitic Per Cent.	Stearic Per Cent.	Oleic Per Cent.	Linoleic Per Cent.	C_{20-22} Unsat. Per Cent.
Outer back (sow)	4·6	21·7	7·6	52·6	12·7	0·8
Inner „ „	4·6	27·7	10·6	42·6	13·2	1·3
Perinephric „	4·7	29·4	16·9	34·5	13·3	1·2
Perinephric (pigs, control diet).	4·4	30·2	20·5	39·9	5·0	—
Perinephric (pigs, control diet+3 per cent. groundnut oil).	2·0	27·4	17·5	43·0	10·1	—

(ii) *Fully Saturated Glycerides present in the Whole Fats*

	Iodine Value of Fat	Total Saturated Acid Content Per Cent. (Mol.)	Fully Saturated Glycerides			Mols. Sat. Acid per Mol. Unsat. Acid in Non-fully Sat. Part
			M.P. °C.	Weight Per Cent.	Mols. Per Cent.	
Outer back (sow)	72·6	33·9	?	2·1	2·2	0·48
Inner „ „	64·6	42·9	60·5	6·6	6·7	0·63
Perinephric „	59·0	51·0	60·5	11·2	11·4	0·81
Perinephric (pigs, control diet).	45·7	55·1	53·0	17·4	17·7	0·83
Perinephric (pigs, control diet+3 per cent. groundnut oil).	55·1	46·9	53·5	13·0	13·2	0·64

(iii) *Component Fatty Acids of the Fully Saturated Glycerides*

	Weight Percentages			Molar Percentages		
	Myristic Per Cent.	Palmitic Per Cent.	Stearic Per Cent.	Myristic Per Cent.	Palmitic Per Cent.	Stearic Per Cent.
Outer back (sow)	0·3	52·2	47·5	0·3	54·7	45·0
Inner „ „	1·4	55·1	43·5	1·6	57·5	40·9
Perinephric „	1·0	55·6	43·4	1·1	58·0	40·9
Perinephric (pigs, control diet).	1·6	59·3	39·1	1·9	61·5	36·6
Perinephric (pigs, control diet+3 per cent. groundnut oil).	2·2	46·0	51·8	2·5	48·4	49·1

3·5 : 1 and 1·5 : 1, the corresponding ratios of these acids in the fully saturated components vary only from about 1·5 : 1 to 1 : 1.

In the fully saturated components of pig depot fats the content of myristic acid is distinctly lower than in those of ox depot fats (*cf.* Table 86), and, correspondingly, the melting points (60·5°) of the pig fat fully saturated glycerides containing about 40 per cent. (mol.) of stearic acid are several degrees higher than those (54–54·5°) of ox depot fully saturated glycerides of similar stearic acid content. The latter may contain, in addition to dipalmitostearin and palmitodistearins, from 12–30 per cent. or even more of myristopalmitostearins, whereas those of pig fats will contain only about 3–6 per cent. of myristopalmitostearins. This typical difference in the fully saturated components of the respective fats is probably also the cause of the characteristic difference in the crystalline forms of the sparingly soluble solid constituents of ox and pig depot fats which is utilised in the Belfield test [27] for distinguishing between beef tallows and lards; it probably also underlies the differences between the respective melting and solidifying points of the solid constituents of lards and tallows (as utilised by Polenske [28]) and the corresponding characteristic differences between the melting points of these saturated glycerides and of the mixed fatty acids contained therein, which were proposed by Bömer[29] as a further means of discrimination between pig and ox depot fats.

Hilditch and Stainsby[9c] prepared a series of progressively hydrogenated fats from the inner back fat of a sow (component acids: myristic 2·8, palmitic 27·3, stearic 14·4, oleic 40·9, linoleic 13·5, C_{20-22} unsaturated 1·1 per cent. mol.). The relation between the fully saturated glyceride and the total saturated acid contents of these fats gave the curve in Fig. 4 (p. 303) which closely follows the observations on the fully saturated glyceride contents of the whole series of natural depot and milk fats.

The tristearin content of the completely hydrogenated fat, and determinations of the fully saturated components of fats hydrogenated to iodine values 18·7 and 10·0, indicated in each case the presence of 15 per cent. of tri-C_{18} glycerides in this pig fat, which contained 5·6 per cent. (mol.) of fully saturated components (component acids: palmitic 54·0, stearic 46·0 per cent. mol.).

Crystallisation of the fully saturated glycerides produced in hydrogenated fats of iodine values 35·8 and 18·7 gave in each case β-palmitodistearin (m.p. 67–67·5°), in amounts corresponding with 76 per cent. and 82 per cent. of the total palmitodistearin present in these fully saturated portions of the fat; it is therefore almost certain that the original pig fat contained β-monopalmito-glycerides unaccompanied by any appreciable quantities of α-monopalmito-glycerides. This was confirmed later by Meara,[44] who compared the melting points of the four polymorphic forms of the products mentioned with those of synthetically prepared α- or β-palmitodistearins.

Ox (sheep, goat) depot fats. Data for the amounts and component acids of the fully saturated glycerides have been given for beef tallows,[9a, 30] for a mutton tallow,[31] for an Indian (Punjab) he-goat depot fat,[32] and for Indian buffalo depot fats.[48b] These are summarised in Table 86.

TABLE 86

(i) *Component Fatty Acids of the Whole Fats* (*Molar Percentages*)

	SATURATED				UNSATURATED				
	C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	C_{18}		C_{20-22}
							OLEIC	DIENOIC	
Ox depot fat, South American.[9a]	9·5	29·2	23·2	*	*	*	37·1	1·0	*
Ox depot fat, South American.[9a]	6·9	25·5	27·4	*	*	*	40·2	—	*
Ox depot fat, South American.[9a]	5·3	32·9	18·2	*	*	*	40·7	2·9	*
Ox depot fat, North American.[9a]	7·5	29·1	13·4	*	*	*	47·6	2·4	*
Shorthorn bullock, perinephric.[30]	3·9†	26·5	23·1	0·7	0·5	2·6	40·4	1·8	0·5
Shorthorn cow, perinephric[30]	3·5	31·0	20·1	0·3	0·7	2·8	39·6	1·8	0·2
Shorthorn heifer, perinephric.[30]	2·5†	28·7	25·4	1·1	0·5	2·0	38·0	1·7	0·1
Buffalo, Indian[48b]	3·9	33·4	31·7	0·5	0·4	2·0	27·8	—	0·3
Buffalo, Indian[48b]	7·4¶	45·6	19·2	0·3	0·8	1·8	22·3	0·7	0·1
Sheep depot fat[31]	5·5	26·2	29·3	*	*	*	34·8	4·2	*
Goat depot fat[32]	7·2‡	27·0	26·8	2·1	*	*	36·9	—	*

* Not estimated.
† Includes traces of lauric acid.
‡ Includes 3·5 (wt.) or 4·7 (mol.) per cent. of lauric acid.
¶ Includes 1·4 per cent. of lauric and 0·4 per cent. dodecenoic acids.

TABLE 86—*continued.*

(ii) *Fully Saturated Glycerides Present in the Whole Fats*

	IODINE VALUE OF FAT	TOTAL SATURATED ACID CONTENT PER CENT. (MOL.)	FULLY SATURATED GLYCERIDES WEIGHT PER CENT.	FULLY SATURATED GLYCERIDES MOLS. PER CENT.	MOLS. SAT. ACID PER MOL. UNSAT. ACID IN NON-FULLY SAT. PART
Ox depot fat, South American [9a]	37·1	61·9	25·3	25·8	0·94
,, ,, ,, ,, ,,	39·3	59·8	25·6	26·0	0·84
,, ,, ,, ,, ,,	42·1	56·4	22·5	22·8	0·75
,, ,, ,, North American	46·6	50·0	13·6	13·9	0·72
Shorthorn bullock, perinephric [30]	44·7	54·2	15·5	15·8	0·78
,, cow, ,,	43·2	54·9	18·0	18·4	0·87
,, heifer, ,,	40·4	57·7	18·1	18·6	0·92
Buffalo, Indian [48b]	26·4	69·5	31·8	32·4	1·22
,, ,, [48b]	23·8	73·9	36·8	37·2	1·41
Sheep depot fat [31]	41·2	61·0	26·0	26·6	0·90
Goat depot fat [32]	33·5	63·1	29·0	29·2	0·92

(iii) *Component Fatty Acids of the Fully Saturated Glycerides*

	WEIGHT PERCENTAGES			MOLAR PERCENTAGES		
	MYRISTIC PER CENT.	PALMITIC PER CENT.	STEARIC PER CENT.	MYRISTIC PER CENT.	PALMITIC PER CENT.	STEARIC PER CENT.
Ox depot fat, South American [9a]	3·3	54·9	41·8	3·9	57·0	39·1
,, ,, ,, ,, ,,	3·9	56·2	39·9	4·5	58·2	37·3
,, ,, ,, ,, ,,	8·1	56·3	35·6	9·3	57·7	33·0
,, ,, ,, North American	6·3	54·0	39·7	7·2	55·8	37·0
Shorthorn bullock, perinephric [30]	14·7	33·6	51·7	17·1	34·7	48·2
,, cow, ,,	10·8	44·0	45·2	12·5	45·4	42·1
,, heifer, ,,	8·3	45·9	45·8	9·6	47·6	42·8
Buffalo, Indian [48b]	7·9	42·0	50·1	9·2	43·7	47·1
,, ,, [48b]	12·5	51·1	36·4	14·4	52·1	33·5
Sheep depot fat [31]	6·1	50·2	43·7	7·1	52·1	40·8
Goat depot fat [32]	2·4	46·1	48·0§	2·9	48·5	45·6

§ Also 3·5 (wt.), 3·0 (mol.) per cent. arachidic acid.

Banks and Hilditch [9a] found evidence that the total C_{18} acid content of ox and sheep depot fats amounted to 62–70 per cent. of the mixed fatty acids, but at the time (1932) of their work the minor proportions of hexa- and tetra-decenoic acids present were not taken into account, with the result that their recorded figures for myristic and oleic acids are somewhat higher than the truth, at the expense of palmitic and tetra- and hexa-decenoic acids. Hilditch and Longenecker, in their 1937 communication,[30] recalculated the earlier figures (*cf.* Chapter III, p. 91) and as a result reached the conclusion that relative constancy of the total C_{18} acids of ox and sheep depot fats at about 60–65 per cent. of the total fatty acids is a strongly marked feature, any increase in stearic acid being closely balanced by diminution of oleic acid. At the same time, and largely independently of the amount of unsaturated acids present, the palmitic acid content of nearly all ox depot fats so far examined lies within the relatively constant limits of 30 (±3) per cent. mol.

These relationships are, of course, exactly similar to those which hold in the case of pig depot fats. The only differences are that ox and sheep depot fats are generally more saturated (i.e. contain less oleo-glycerides) than those of the pig, and that they also contain definitely more myristic acid in combination as a minor component.

THE COMPONENT GLYCERIDES OF OX AND SHEEP FATS

The composition of the fully saturated glycerides of ox and sheep depot fats also resembles that of the corresponding parts of pig depot fats (except for higher myristic acid contents). In the eight cases on record, stearic acid forms from 37 to 43 per cent. (mol.) of the component acids in six instances, the remaining two having 33 and 48 per cent. of stearic acid in the fully saturated components. Palmitic and myristic acids thus bear a ratio to stearic acid varying between 2 : 1 and 1 : 1 in the fully saturated components. This tendency towards constancy would result from the hydrogenation envisaged as operating during the formation of these depot fats, since oleodipalmitins would tend to reach complete saturation in greater amounts than palmitodioleins.

Since the later, more detailed studies of pig, ox and sheep depot fats (*cf.* below) have suggested that triolein is not present in significant amounts, the data for the fats in Tables 85 and 86 permit the proportions of fully saturated, mono-oleo- and di-oleo-glycerides in these instances to be approximately calculated (Table 87).

TABLE 87

OX AND SHEEP DEPOT FATS	FULLY SATURATED PER CENT. (MOL.)	MONO-" OLEO "-DISATURATED PER CENT. (MOL.)	DI-" OLEO "-MONOSATURATED PER CENT. (MOL.)
Ox depot fat, South American [9a]	26	34	40
,, ,, ,, ,, ,,	26	27	47
,, ,, ,, ,, ,,	23	22	55
,, ,, ,, North America	14	22	64
Shorthorn bullock, perinephric [30]	16	31	53
,, cow, ,,	18	28	54
,, heifer, ,,	18	28	54
Buffalo, Indian [48b]	32	44	24
,, ,, [48b]	37	47	16
Sheep depot fat [31]	27	31	42
Goat depot fat [32]	29	31	40
Pig, perinephric [9b]	18	30	52
Sow, perinephric [9b]	11	30	59
,, inner back	7	15	78
,, outer back	2	—	95*

* 3 per cent. tri-" olein."

STUDY OF "STEARIC-RICH" ANIMAL DEPOT FATS BY THE ACETONE CRYSTALLISATION PROCEDURE

A group of seven pig, sheep and ox depot fats in which the stearic acid ranged from 14 to 28 per cent. (mol.), whilst the oleic acid correspondingly ranged from 46 to 23 per cent. (mol.), of the total component acids has now been studied in detail by first resolving each fat into three or more fractions by crystallisation, and then determining the component acids in each fraction (together with their fully saturated glycerides and tri-C_{18} glycerides where requisite), by which means a fairly exact statement can be made of the proportions of the chief component glycerides present. The procedure has been described in detail (Chapter VI, pp. 241, 244) in its application to solid vegetable fats, but the importance of further study of animal fats, and the existence of certain minor complications in its application to this class of fats, perhaps justifies its further illustration here. For this purpose the first study of an animal fat in this manner—that of an English ox depot fat by Hilditch and S. Paul [18a]—may be described.

The fat, from the perinephric tissue of a Shorthorn heifer, had the following component acids:

	Per Cent. (Wt.)	Per Cent. (Mol.)
Lauric	0·5	0·7
Myristic	2·7	3·2
Palmitic	30·4	32·2
Stearic	23·7	22·6
Tetradecenoic	0·4	0·5
Hexadecenoic	1·7	1·8
Oleic	38·6	37·1
Octadecadienoic	2·0	1·9

By a series of crystallisations from acetone, it was finally resolved into three fractions A, B, C (of increasing solubility), the component acids of each of which were determined with the results given in Table 88A.

TABLE 88A. *COMPONENT ACIDS OF FRACTIONS A, B, C OF OX DEPOT FAT*

	A	B	C	Mean for Whole Fat
Weight of fraction (g.)	244	413	368	
Iodine value	15·9	37·5	57·4	
Glycerides per cent. (wt.)	23·8	40·3	35·9	
,, ,, (mol.)	23·9	40·3	35·8	
Component acids (per cent. mol.):				
Lauric	—	0·2	0·4	0·25
Myristic	1·5	2·6	3·0	2·4
Palmitic	46·5	31·7	26·5	33·4
Stearic	30·3	24·7	11·7	21·4
Arachidic	4·8	0·3	0·1	1·3
Tetradecenoic	0·4	0·4	0·9	0·6
Hexadecenoic	1·1	1·6	2·7	1·9
Oleic	15·4	37·4	45·8	35·2
Octadecadienoic	—	1·1	8·8	3·5
C_{20-22} unsaturated	—	—	1·1	0·05

The proportions and fatty acid compositions of the fully saturated glycerides present in fractions A and B were determined; tristearin present in the fully saturated components was also estimated. A portion of each fraction was also completely hydrogenated and the tristearin contents of the products determined. The data obtained were briefly as follows:

	A	B	C
Fully saturated glycerides:			
Per cent. (mol.) of fraction	60·0	7·4	—
Per cent. tri-C_{18} glycerides present	3·0	—	—
Tri-C_{18} glycerides:			
Per cent. (mol.) of fraction	17·7	15·1	9·3

A full description of the methods of evaluation of the data obtained in each fraction has been given earlier (Chapter VI, pp. 246–248), and the details in the present instance are explained in the original paper.[18a] In applying these calculations to animal depot fats, however, certain features cause somewhat more difficulty than, for example, arises in the case of seed fats which contain, substantially, only oleic and linoleic, stearic and palmitic acid as component acids.

In animal depot fats the number of minor component acids is greater than in many seed fats, and, unfortunately, includes, amongst others, about 2–3 per cent. of hexadecenoic acid (and traces of tetradecenoic acid), belonging simultaneously to the unsaturated group and to the group of non-C_{18} acids. In relation to the three major components (palmitic 33, stearic 21, oleic 35 (" oleic " 39), amounting together to 93 per cent. of the component acids) the quantity of any one of the minor components is almost insignificant; but it must be remembered that each molecule of a minor component will be associated almost invariably with two molecules of one or other of the three major components in a mixed triglyceride molecule, so that the total percentage of triglycerides involved is not of the order of 7 per cent., but about 20 per cent., of the whole fat. Whilst it is desirable to draw attention to this feature, it should equally be pointed out that the data are entirely valid from the point of view of the distribution of saturated non-C_{18} and C_{18} acids in the mixed glycerides of the depot fat, and that the great predominance of palmitic acid in the former class ensures that the conclusions drawn later cannot be, in point of fact, very far from the actual state of affairs. It is perhaps not unreasonable to remark upon the fact that the presence of a number of minor component acids is a bugbear of detailed study of component glycerides in natural fats; in the rare absence of these, it is now possible to give an almost exact statement of the component glycerides present in a fat containing only three fatty acids.

For the present purpose, myristic and lauric are included with palmitic glycerides, and arachidic with stearic glycerides, whilst the traces of unsaturated C_{20} and C_{22} acids are included in the " oleic " (i.e. unsaturated C_{18}) acid group. Hexadecenoic (and tetradecenoic) glycerides, which fall in the unsaturated non-C_{18} category, have been included also with palmitic glycerides, since on hydrogenation (for the tri-C_{18} glyceride determinations) they yield palmito- (or myristo-) glycerides. Accordingly, in terms of non-C_{18} (" palmitic "), stearic, and " oleic " derivatives, the data in Table 88A, together with those for the fully saturated glycerides and contents of tri-C_{18} glycerides, may be amplified as shown in Table 88B.

TABLE 88B. *GLYCERIDE CATEGORIES (PER CENT. MOL.) PRESENT IN FRACTIONS A, B, AND C OF OX DEPOT FAT*

	A		B		C	Whole Fat
Glycerides	23·9		40·3		35·8	100·0
Component acids (increments):						
Palmitic	11·85		14·7		12·0	38·55
Stearic	8·35		10·1		4·25	22·7
" Oleic "	3·7		15·5		19·55	38·75
	Fully Sat.	Mixed	Fully Sat.	Mixed		
Component glycerides (increments):						
Tri-C_{18}	0·4	3·8	—	6·1	3·3	13·6
Palmitodi-C_{18}	5·8	0·8	—	24·9	29·0	60·5
Dipalmitomono-C_{18}	5·4	4·9	2·4	6·3	3·5	22·5
Tripalmitin	2·8	—	0·6	—	—	3·4
Mono-" oleo "-disaturated	—	8·0	—	28·1	12·9	49·0
Di-" oleo "-monosaturated	—	1·5	—	9·2	22·9	33·6

Consideration of the data in Table 88B led to the statement of component glycerides in the fractions of the original fat, and therefrom in the whole original fat, shown in Table 88C.

TABLE 88C. *PROBABLE COMPONENT GLYCERIDES (PER CENT. MOL.) OF THE OX DEPOT FAT*

	A		B		C	Whole Fat	
	Fully Sat.	Mixed	Fully Sat.	Mixed			(In Round Numbers)
Fully saturated glycerides (17·4 per cent.):							
Tripalmitin	2·8	—	0·6	—	—	3·4	3
Dipalmitostearin	5·4	—	2·4	—	—	7·8	8
Palmitodistearin	5·8	—	—	—	—	5·8	6
Tristearin	0·4	—	—	—	—	0·4	†
Mono-" oleo "-disaturated glycerides (49·0 per cent.):							
" Oleo "-dipalmitin	—	4·9	—	6·3	3·5	14·7	15
" Oleo "-palmitostearin	—	0·8	—	21·8	9·4	32·0	32
" Oleo "-distearin	—	2·3	—	—	—	2·3	2
Di-" oleo "-monosaturated glycerides (33·6 per cent.):							
Palmitodi-" oleins "	—	—	—	3·1	19·6	22·7	23
Stearodi-" oleins "	—	1·5	—	6·1	3·3	10·9	11
Tri-" oleins "	—	—	—	—	*	*	*

* Traces of tri-" oleins," probably not exceeding 1 per cent. of the fat, may be present.

† Tristearin is present to the extent of less than 1 per cent. of the fat.

In addition to the English heifer fat described above, there have now been studied by the acetone crystallisation procedure the component glycerides of two Indian cow depot fats (Hilditch and Murti[18b]), of external and perinephric tissue fats from a pig (Hilditch and Pedelty[19]), and of external and perinephric tissue fats from a ewe (Hilditch and Zaky[20]). This series as a whole lends itself to consideration with respect to the manner in which the proportions of the different groups of mixed glycerides vary according to the proportions of oleic, stearic, and palmitic acids present in the whole fats. For this purpose the data are arranged in Table 89A with the fats in general decreasing order of total unsaturation.

TABLE 89A. *COMPONENT GLYCERIDES OF PIG, SHEEP, AND OX DEPOT FATS (PER CENT. MOL.)*

	EWE[20] EXTERNAL	PIG[19] BACK	PIG[19] PERINEPHRIC	EWE[20] PERINEPHRIC	HEIFER[18a] ENGLISH	COW[18b] CALICUT	COW[18b] BOMBAY
Component acids:							
Myristic (+C_{12})	3·8	1·3	1·8	3·0	2·6	5·7	5·9
Palmitic	31·5	29·0	31·1	27·1	33·4	33·4	40·8
Stearic	14·5	13·8	17·6	25·6	21·4	27·9	25·5
Arachidic	0·4	—	—	1·5	1·3	0·5	0·7
Hexa-(+tetra-)decenoic	1·2	2·7	2·4	2·0	2·5	1·9	2·8
Oleic	45·8	43·9	40·6	37·1	35·2	29·0	22·9
Octadecadienoic	2·1	7·2	5·3	3·3	3·5	1·5	1·1
Unsaturated C_{20-22}	0·7	2·1	1·2	0·4	0·1	0·1	0·3
Component glycerides:							
Fully saturated:							
Tripalmitin	Trace	1	—	Trace	3	—	3
Dipalmitostearin	3	2	4	4	8	16	23
Palmitodistearin	2	2	5	10	6	12	10
Tristearin	—	—	—	Trace	—	—	—
Mono-" oleo "-disaturated:							
" Oleo "-dipalmitin	13	5	9	5	15	11	18
" Oleo "-palmitostearin	28	27	34	41	32	38	34
" Oleo "-distearin	1	—	—	2	2	2	—
Di-" oleo "-monosaturated:							
Palmitodi-" olein "	46	53	40	25	23	17	11
Stearodi-" olein "	7	7	5	13	11	3	1
Tri-" oleins "	0	3	3	0	0	0	0

It will be seen that decrease in oleic acid content is accompanied by generally corresponding increases in stearic acid content until the latter reaches about 28 per cent., beyond which further diminution in oleic acid is apparently compensated for by increases beyond the normal (30 per cent.) proportion of palmitic acid. Thus the palmitic acid content of the Bombay cow fat, and also the combined palmitic and myristic acid content of the Calicut cow fat, are abnormally high ; this incidentally complicates to some extent comparisons in relation to the development of mixed stearo-glycerides with increasing general saturation in these fats. Nevertheless it is instructive to compare the relative proportions of palmitodi-" oleins," " oleo "-palmitostearins, and palmitodistearins as the proportion of stearic acid in the whole fat increases (Table 89B).

TABLE 89B. *RELATIVE PROPORTIONS OF PALMITODI-" OLEINS," " OLEO "-PALMITOSTEARINS, AND PALMITODISTEARINS*

	PIG BACK	EWE EXTERNAL	PIG PERINEPHRIC	OX ENGLISH	EWE PERINEPHRIC	COW CALICUT	COW BOMBAY
C_{18} fatty acids:							
Stearic	13·8	14·5	17·6	21·4	25·6	27·9	25·5
Oleic + octadecadienoic	51·1	47·9	45·9	38·7	40·4	30·5	24·0
Palmitodi-C_{18} glycerides (increments per cent.):							
Palmitodi-" oleins "	53	46	40	23	25	17	11
" Oleo "-palmitostearins	27	28	34	32	41	38	34
Palmitodistearins	2	2	5	6	10	12	10
	82	76	79	61	76	67	55
Palmitodi-C_{18} glycerides (per cent.):							
Palmitodi-" oleins "	65	61	51	38	33	25	20
" Oleo "-palmitostearins	33	37	43	52	54	57	62
Palmitodistearins	2	2	6	10	13	18	18

In the last three lines of Table 89B the amount of each of the respective glycerides is expressed as a percentage of the total monopalmito-glycerides of the fat (the term *monopalmito-* in the present connotation including the minor amounts of monomyristo-glycerides present). The progressive change in the relative proportions of the three types of palmitodi-C_{18} glycerides thus becomes strikingly evident, and is a very strong argument in favour of the hydrogenation hypothesis which has been put forward (*cf.* p. 304) to account for the varying proportions of fully saturated glycerides in these animal fats. It will be observed that, as the proportions of oleic acid decline, the most noticeable change in the glycerides is at first a steady increase in the percentage of " oleo "-palmitostearin, whilst the fully saturated palmitodistearins also commence to augment, but do not exceed 18 per cent. in the extreme cases ; meantime the percentage of " oleo "-palmitostearin in the monopalmito glycerides rises from 33 per cent. in the most unsaturated fat to over 60 per cent. in the most saturated fat in the series.

A somewhat similar comparison may be made in regard to the relative proportions of " oleo "-dipalmitin and dipalmitostearin in the dipalmito-mono-C_{18} group of glycerides. Here, however, the total proportion of the dipalmito-glycerides is partly dependent upon the palmitic acid content in the whole fats ; the latter rises considerably above the average in the Indian cow depot fats with consequent increase in the amount of dipalmito-glycerides at the expense of the monopalmitodi-C_{18} group. Apart from increased proportions of dipalmito-glycerides from this cause, however, a tendency has been observed[19] for this group to increase in amount with increasing general saturation in the fats as a whole. The relevant data on this aspect for the seven fats for which information is now available are summarised in Table 89C ; in this case, since the minor quantities of lower saturated acids present are perforce included with palmitic acid in the evaluation of the main component glycerides, comparison is made with the combined amount of palmitic, myristic and lauric acids in the total acids of the fats.

TABLE 89C. *RELATIVE PROPORTIONS OF " OLEO "-DIPALMITIN AND DIPALMITOSTEARIN*

	PIG BACK	EWE EXTERNAL	PIG PERINEPHRIC	OX ENGLISH	EWE PERINEPHRIC	COW CALICUT	COW BOMBAY
Fatty acids:							
Palmitic (+C_{14}, C_{12})	30·3	35·3	32·9	36·0	30·1	39·1	46·7
Stearic	13·8	14·5	17·6	21·4	25·6	27·9	25·5
Total unsaturated	55·9	49·8	49·5	41·3	42·8	32·5	27·1
Dipalmitomono-C_{18} glycerides (increments per cent):							
" Oleo "-dipalmitins	5	13	9	15	5	11	18
Dipalmitostearins	2	3	4	8	4	16	23
	7	16	13	23	9	27	41
Dipalmitomono-C_{18} glycerides (per cent.):							
" Oleo "-dipalmitins	71	81	69	65	56	41	44
Dipalmitostearins	29	19	31	35	44	59	56

The total amount of dipalmito-glycerides in the depot fats bears a general, though somewhat irregular, relationship to the proportion of palmitic acid present in the whole fat ; but the relative proportions of " oleo "- and stearodipalmitins are, as in the monopalmito-di-C_{18} glycerides, governed entirely by the proportion of stearic and unsaturated acids present and thus again support the view that production of the more saturated component glycerides involves hydrogenation of preformed " oleo "-glycerides—in this case " oleo "-dipalmitins.

The presence of perhaps 2–3 per cent. of tripalmitin in some of the fats in Table 89A which contain large proportions of stearic as well as palmitic acid is unusual. Tripalmitin has elsewhere only been reported in cases in which the saturated acids of a natural fat consist almost wholly of palmitic acid (e.g. olive oil, palm oil, rabbit depot fat), and, when stearic and palmitic acids are both present in quantity (as in cacao butter and many other seed fats), any fully saturated components have been found to consist of mixed palmitostearins. The tripalmitin in these " stearic-rich " depot fats is explicable, however, on the above " hydrogenation " hypothesis, since hexadecenoic acid is a minor component thereof, and saturation of any hexadeceno-palmitins present in the fat would, of course, yield tripalmitin.

Riemenschneider *et al.*[49] have also (1945) described the resolution of tallows and lards into seven fractions by crystallisation from acetone between −20° and −45°. From the component acids in each fraction (determined from iodine value, and absorption spectra after alkali-isomerisation, as saturated, oleic and octadecadienoic) the component glycerides were calculated on the assumption that only binary mixtures of fully saturated, mono-" oleo "-disaturated, di-" oleo "-monosaturated, and tri-unsaturated glycerides were respectively present. These authors note that tallows contain much more fully saturated and mono-" oleo "-glycerides than lards, and also conclude that the tri-unsaturated glyceride contents of lards are definitely greater than hitherto suggested in the literature.

Arithmetical computation of component glycerides in " stearic-rich" animal depot fats. It was shown in the preceding Chapter (pp. 249–

255) that in many cases of " evenly distributed " glyceride structure encountered in vegetable fats the experimentally observed results can be simulated, at least so far as the major component glycerides are concerned, by calculations based upon the proportions of the component acids of the fat, and depending upon arithmetical partition of oleic (or other major unsaturated) acid between the rest of the component acids. It is evident that such a calculation cannot reproduce the observed proportions of the various individual mixed glycerides in the " stearic-rich " animal depot fats which we are now considering.

It was noticed,[18a, 18b, 20] however, in a number of these fats that, after deducting the palmitic and stearic acids observed to be present in the fully saturated constituents from the total amounts of these acids in the mixed fatty acids of the whole fats, partition of the " oleic " acid between the rest of the palmitic and stearic acids gave figures for the various mixed " oleo "-saturated glycerides in fairly close agreement with the observed values. This is illustrated for the seven fats discussed in Table 89A in Table 90 (p. 324). It will be seen that the values for the mixed " oleo "-glycerides found by analysis (*a*) are in fact very closely reproduced by this form of computation (*b*) in the four fats which have contents of more than 20 per cent. of stearic acid ; the accordance is not quite so well marked in some instances (especially in some of the " oleo "-dipalmitin figures) in those fats which contain only 14–17 per cent. of stearic acid.

On the other hand, the " computed " data, based upon arithmetical partition of the unsaturated acids between all the palmitic and stearic acids in these fats (i.e. taking no account of the amounts of saturated acids present in the form of fully saturated glycerides) are shown in columns (*c*) of Table 90. Whilst these accord moderately well with the observed figures in the fats poorest in stearic acid (pig and ewe external fats), they of course become increasingly disaccordant as the amount of fully saturated glycerides becomes more prominent. The discrepancies between the computed values (*c*) and the observed values (*a*) are most extreme with " oleo "-palmitostearin and palmitodi-" olein ".

The accordance between the values (*b*) computed after allowance for the observed fully saturated glycerides and the observed values (*a*) might be expected if, in the suggested biohydrogenation process, the hydrogen molecules are attached in indiscriminate fashion to some of the double bonds of a preformed mixture of oleo-glycerides assembled on the lines of " even distribution." Since it is quite possible that such preformed oleo-glycerides contain a minor proportion of stearic acid (such as usually accompanies palmitic acid when the latter is a major component acid in a natural fat), the regularities due to superimposing the partial hydrogenation upon the preformed oleo-glycerides may not be developed clearly until the amount of stearo-glycerides thus formed becomes fairly large ; this may account for the less good accordance in the calculated and observed figures for mixed oleo-saturated glycerides of body fats containing 15 per cent. or less of stearic acid.

Arithmetical computation of the chief mixed glycerides of a " stearic-rich " animal body fat by this method would thus involve separate determination of the fully saturated glycerides and their component acids. This can be avoided, however, by employing the graph in Fig. 4 (p. 303) to give an approximate measure of the proportion of fully saturated glycerides in

TABLE 90. *OBSERVED AND "COMPUTED" VALUES (PER CENT. MOL.) OF COMPONENT GLYCERIDES OF "STEARIC-RICH" ANIMAL DEPOT FATS*

	Pig[19]						Ewe[20]						Cow								
	External			Perinephric			External			Perinephric			English[18a]			Calicut[18b]			Bombay[18b]		
Component acids:																					
Palmitic *	33·0			35·3			36·5			32·1			38·5			41·0			49·5		
Stearic †	13·8			17·6			14·9			27·1			22·7			28·4			26·2		
Oleic §	53·2			47·1			48·6			40·8			38·8			30·6			24·3		
	Found	"Computed"		Found	"Computed"		Found	"Computed"		Found	"Computed"		Found	"Computed"		Found	"Computed"		Found	"Computed"	
Component glycerides:	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)
Tripalmitin	1	(1)	—	—	(—)	—	—	(—)	—	—	(—)	—	3	(3)	—	—	(—)	—	3	(3)	—
Dipalmitostearin	2	(2)	—	4	(4)	—	3	(3)	—	4	(4)	—	8	(8)	—	16	(16)	10	23	(23)	29
Palmitodistearin	2	(2)	—	5	(5)	—	2	(2)	—	10	(10)	—	6	(6)	—	12	(12)	3	10	(10)	1
"Oleo"-dipalmitin	5	11	12	9	14	15	13	20	26	5	4	2	15	11	20	11	13	13	18	21	19
"Oleo"-palmitostearin	27	26	34	34	31	46	28	27	26	41	47	76	32	40	66	38	40	70	34	34	49
"Oleo"-distearin	—	—	—	—	—	—	1	—	—	2	—	—	2	—	—	2	—	—	—	—	—
Palmitodi-"olein"	53	43	41	40	34	30	46	35	32	25	23	16	23	23	12	17	13	4	11	7	2
Stearodi-"olein"	7	8	8	5	8	6	7	11	14	13	10	5	11	8	2	3	5	—	1	2	—
Tri-unsaturated	3	7	5	3	4	3	0	2	2	0	2	1	—	—	—	0	1	—	0	—	—

* Including minor component myristic, tetradecenoic and hexadecenoic acids.

† Including minor component arachidic acid.

§ Including minor component octadecadienoic and unsaturated C_{20-22} acids.

an animal body fat from the proportion of saturated acids in the total component acids. Further, for the purposes of approximate calculation, these fully saturated glycerides may be assumed to be made up of 60 per cent. palmitic and 40 per cent. stearic acid (*cf.* pp. 314, 317). The oleic acid present may then be partitioned, as before, between the remaining palmitic and stearic, and the other unsaturated, acids. By this means a reasonable approximate estimate of the chief component glycerides of a " stearic-rich " animal depot fat can be made directly from the fatty acid compositions of such fats as a whole, without recourse to actual determination of fully saturated glycerides and their component acids.

Kangaroo body fat. Except for the fats of the domestic animals discussed in the preceding pages, only one other " stearic-rich " animal depot fat has yet been studied by the detailed acetone crystallisation procedure, namely, the fat from the adipose tissues of a young adult Great Grey Kangaroo (*Macropus major*). Hilditch and Sime [33] separated a small specimen of this fat into two fractions by crystallisation from acetone at −10°, from which an approximate idea of the component glycerides was obtained.

The component acids were lauric 0·2, myristic 5·6, palmitic 27·1, stearic 13·5, arachidic 1·3, tetradecenoic 0·5, hexadecenoic 2·9, oleic 44·0, octadecadienoic 2·5, and unsaturated C_{20-22} 2·4 per cent. (mol.). The glycerides, in spite of the somewhat high content of stearic acid, appeared to contain only 0·5 per cent. of palmito-stearins, the main components being 47 per cent. palmitodi-" oleins " and 42 per cent. " oleo "-palmitostearins, with about 9 per cent. of oleodipalmitin and 2 per cent. of stearodi-" olein." (It should be noted, however, that these figures were obtained only from the component acids present in each crystallised fraction, insufficient material preventing an actual determination of the fully saturated glycerides in the less soluble fraction from acetone.)

The position as regards our knowledge of the natural glycerides present in animal depot fats is undoubtedly more satisfactory than it was 15–20 years ago ; but the description which has now been given will show the reader that, apart from a fairly adequate knowledge of the technically important classes of lards and tallows, there is still room for much investigation into the component glycerides of other classes of depot fats. The study of depot fats from a much wider range of animals and birds than has hitherto been possible is necessary before we can even be certain that such fats are confined to the types which have already been indicated by the work undertaken up to the present. The writer has endeavoured in the present chapter to give a fair representation of the information already available, but the somewhat fragmentary character of the materials studied, together with the number of animal species of which the depot fats have not yet received attention, should always be borne in mind.

MILK FATS

In spite of the great number of analytical investigations which have been undertaken in order to determine on the one hand the characteristic values of butter fats (mainly in connection with their content of so-called volatile acids), and on the other hand the composition of the mixed fatty acids in greater or less detail, there is a relative lack of work with reference to the actual nature of the glycerides present in these fats.

The first serious attempts to examine the glyceride structure of a milk fat took, as usual, the form of fractional crystallisation studies, and were due to Amberger.[34] This investigator succeeded in isolating small quantities of palmitodistearin (m.p. 62·8°) and stearodipalmitin, and also oleodipalmitin and butyropalmito-olein; whilst he indicated that the amount of triolein present was of the order of only 2 per cent. Tristearin and butyrodiolein were also considered possibly to be present. The mixed glycerides isolated evidently amounted only to a comparatively small proportion of the whole of the fat.

In 1928, Arup [35] separated samples of Irish butter fat into a number of ractions by removing solid components which crystallised out from the fat as a whole on standing at various temperatures, and determined the Reichert-Meissl, Kirschner, iodine, etc., values of the separated fractions. The results led him to conclude that the low molecular weight acids, and also the higher saturated acids, are distributed more or less evenly throughout the whole of the fat, and he found little evidence of the presence of simple triglycerides such as tributyrin, triolein, etc.

Somewhat fuller information on the component glycerides of milk fats has resulted from the examination of a number of cow milk fats, and of specimens of buffalo, goat, sheep, and camel milk fats by the semi-quantitative permanganate-acetone oxidation procedure, which leads to the isolation and determination of the fully saturated components, and the proportions of the saturated fatty acids therein combined.

Cow milk fats. The fully saturated glycerides present in fourteen cow milk fats were examined in this way by Hilditch and co-workers. Eight of these were from animals from England, New Zealand, or India, fed on a natural diet of grass or on ordinary winter stall diet; the remaining six were from animals which had received, in addition to basal stall feed, certain amounts of specific fatty oils or oil cakes. The component acids in these fourteen milk fats were discussed in detail in Chapter III (pp. 113, 115, 120, Tables 43A, 43B, 44B), whilst their fully saturated glyceride contents were compared with the proportions of saturated acids in the total fatty acids of each fat in Table 80 of this Chapter (p. 299). The studies of glyceride structure of these cow milk fats included in some cases determination of the component acids of the fully saturated components, but in others were confined to ascertaining the percentage proportions and mean saponification equivalents of the latter group.

The more completely examined fats included two market samples of New Zealand butter,[36] two English fats and a New Zealand fat from cows fed on normal pasture or winter (stall) diets,[11] an Indian ghee from cows fed on pasture,[37] and two English milk fats from cows on a winter stall diet supplemented by either coconut or soya bean cake.[11] The more important data obtained are summarised in Table 91A (minor unsaturated component

TABLE 91A. *GLYCERIDE STRUCTURE OF EIGHT COW MILK FATS*

No. in Table	Cow Milk Fat
E 1929	English, spring pasture, 1929.
E 1928	,, autumn feed, 1928.
NZ (i)	New Zealand, market sample, 1927.
Indian	Indian, pasture feed, 1930.
NZ (ii)	New Zealand, market sample, 1927.
NZ (iii)	,, ,, spring pasture, 1928.
ES	English, stall feed, 1929 (soya bean cake in diet).
EC	,, ,, ,, ,, (coconut cake in diet).

(i) *Component Fatty Acids of the Whole Fats* (*Molar Percentages*)

Fat	E 1929	E 1928	NZ (i)	Indian	NZ (ii)	NZ (iii)	ES	EC
Butyric acid	8·9	8·4	8·4	6·9	9·2	9·2	9·6	9·0
n-Hexanoic acid	2·7	3·5	3·9	4·0	3·7	3·4	3·0	3·9
n-Octanoic ,,	2·0	2·7	1·3	2·2	1·4	2·2	2·8	1·7
n-Decanoic ,,	3·0	2·9	2·8	4·9	2·7	4·2	5·1	4·3
Lauric ,,	4·7	4·1	4·6	6·7	3·7	4·7	7·5	8·3
Myristic ,,	10·9	7·2	11·0	10·9	10·2	11·5	10·7	17·2
Palmitic ,,	24·3	27·1	26·2	26·8	25·7	25·0	23·7	24·1
Stearic ,,	5·4	6·4	7·1	5·5	10·2	9·5	6·7	3·9
Arachidic ,,	—	0·7	0·8	—	0·5	0·5	0·9	—
Oleic ,,	34·6	33·9	30·8	28·4	28·9	26·1	27·0	25·7
Octadecadienoic acid	3·5	3·1	3·1	3·7	3·8	3·7	3·0	1·9

(ii) *Fully Saturated Glycerides Present in the Whole Fats*

	E 1929	E 1928	NZ (i)	Indian	NZ (ii)	NZ (iii)	ES	EC
Whole Fats:								
Iodine value	41·6	41·3	39·4	36·0	38·0	34·5	34·8	31·6
Total saturated acid content (per cent. mol.).	61·9	63·0	66·1	67·9	67·3	70·2	70·0	72·4
Fully saturated glycerides:								
per cent. (wt.)	24·3	25·4	29·2	31·7	31·3	37·4	35·0	38·5
per cent. (mol.)	27·2	29·1	31·5	33·7	33·8	39·6	38·2	41·3
Mols. saturated acids per mol. unsaturated acid in non-fully saturated part.	0·94	0·92	1·03	1·07	1·04	1·07	1·07	1·11

(iii) *Component Fatty Acids of the Fully Saturated Glycerides* (*Molar Percentages*)

	E 1929	E 1928	NZ (i)	Indian	NZ (ii)	NZ (iii)	ES	EC
Butyric acid	11·4	11·7	10·5	11·2	11·0	11·2	9·2	9·2
n-Hexanoic acid	5·1	5·3	4·9	5·1	6·5	4·6	6·4	5·8
n-Octanoic ,,	2·7	2·2	5·0	0·5	1·8	3·4	3·1	2·8
n-Decanoic ,,	5·3	4·2	3·1	4·4	3·3	5·1	6·3	6·9
Lauric ,,	6·0	5·2	4·7	6·1	4·1	5·3	6·4	11·1
Myristic ,,	15·1	13·2	17·0	15·5	17·9	14·9	19·6	20·1
Palmitic ,,	39·5	43·1	39·3	43·0	39·6	39·9	36·1	35·4
Stearic ,,	14·9	15·1	15·2	14·2	15·8	15·6	12·6	8·7
Arachidic ,,	—	—	0·3	—	—	—	0·3	—

acids were not determined in any of these analyses). Less complete data for six English cow milk fats, two of which were from normally stall-fed animals, whilst the others were for cows which had received in addition eight ounces per day of either linseed, rape, or cod liver oil, have also been recorded [22] (Table 91B).

The data for all fourteen fats show consistently that the content of fully saturated glycerides is, within close limits, simply a function of the relative proportions of saturated and unsaturated acids in the whole fat, irrespective of the nature of the saturated acids, or of abnormalities in the component fatty acids caused by ingestion of specific fatty acids (*cf.* Chapter III, p. 120). In this respect butter fats resemble lards and tallows very closely and, indeed, when the relationship between fully saturated glyceride

TABLE 91B. *FULLY SATURATED GLYCERIDES (AMOUNTS AND MEAN EQUIVALENTS) OF SIX COW MILK FATS*

OIL FED TO COW	WHOLE FAT			FULLY SATURATED GLYCERIDES		
	I.V.	SAP. EQ.	SATURATED ACIDS PER CENT. (MOL.)	PER CENT. (WT.)	PER CENT. (MOL.)	SAP. EQ.
Control	34·5	239·7	71·4	37·1	40·4	221·0
,,	34·9	244·2	69·1	31·1	34·2	224·5
Linseed	46·0	249·0	61·3	22·2	24·8	222·4
Rape	44·5	251·2	59·4	22·4	25·3	225·0
Cod liver	51·7	264·2	53·5	15·3	17·2	235·7
,,	54·1	266·0	50·6	12·8	14·6	235·1

content and total saturated acid content is plotted as a graph, the curve obtained (*cf.* this chapter, Fig. 4, p. 303) is a prolongation of that given by the corresponding data for the pig and cattle reserve fats. Notably, in spite of the marked differences in the relative amounts of their component acids as compared with normal butters, the milk fats from cows which had received cod liver oil in the diet still conform to this typical relationship. Indeed, their positions on the curve in Fig. 4 emphasise the fact that, from this aspect of glyceride structure, there is complete uniformity in type between cow milk fats and ox, sheep, or pig depot fats.

In the fourteen cow milk fats which have been examined, the molar proportions of fully saturated components range from 14·6 to 41·3 per cent., so that the non-fully saturated glycerides present in these fats vary in amount from 59 to 85 per cent. There is little or no evidence that triolein is present in any great amount in normal butter fats, and considerable indirect evidence against this possibility (*cf.* Amberger [34]). Consequently in most of the butters studied the glycerides are probably made up of fully saturated components with mono-" oleo "- and di-" oleo "-glycerides in proportions near to those given in Table 92.

TABLE 92. *PROBABLE GENERAL COMPOSITION OF COW MILK FATS*

	FULLY SATURATED PER CENT. (MOL.)	MONO-" OLEO "-DISATURATED PER CENT. (MOL.)	DI-" OLEO "-MONOSATURATED PER CENT. (MOL.)
English, stall-fed, 1934 (cod liver oil in diet)	14·6	23·0	62·4
,, ,, ,, ,, ,, ,,	17·2	26·1	56·7
,, ,, ,, (linseed oil in diet)	24·8	34·3	40·9
,, ,, ,, (rape oil in diet)	25·3	27·6	47·1
,, spring pasture, 1929	27·2	33·0	39·8
,, autumn feed, 1928	29·1	31·0	39·9
New Zealand, market sample, 1927	31·5	35·8	32·7
Indian, pasture fed, 1930	33·7	36·5	29·8
New Zealand, market sample, 1927	33·8	35·0	31·2
English, stall-fed, 1934	34·2	38·9	26·9
,, ,, 1929 (soya bean cake in diet)	38·2	34·0	27·8
New Zealand, spring pasture, 1928	39·6	33·3	27·1
English, stall-fed, 1934	40·4	33·4	26·2
,, ,, 1929 (coconut cake in diet)	41·3	33·9	24·8

These general characteristics of butter fat glyceride structure have a practical bearing on the variation in the " melting point " or softness of butters. It is evident that increase in oleic acid content of butter, according to the above data, will be reflected in a disproportionate increase in softness, since not only is the ratio of unsaturated to saturated acids increased in the saturated-unsaturated mixed glycerides, but the quantity of the latter increases considerably with augmentation of the oleic acid. Leaving out of consideration the six fats from animals which had received fatty oils or seed cakes as part of their diets, it will be noticed from Table 92 that the remaining eight milk fats from cows on normal diets differ to a considerable extent in their component glycerides, and therefore in their physical characteristics of hardness or softness. This difference is not very marked so far as the mono-" oleo "-disaturated glycerides (which melt somewhat above room temperature) are concerned, for these are moderately constant, with a range of about 33–39 per cent. of the total fats. The fully saturated components vary from 27 to 40 per cent., however, with a corresponding variation in the *di-" oleo "-monosaturated glycerides* of almost the same extent. Consequently, increase in unsaturation (oleic acid content) of a milk fat has a dual effect on the consistency of the butter : not only is the amount of the highest melting (i.e. fully saturated) components reduced, but that of the di-" oleo "-glycerides (which are liquid at the ordinary temperature) is increased to approximately the same extent as the reduction in fully saturated components.

It was pointed out earlier (Chapter III, pp. 115, 116) that the amounts of the different component fatty acids present in milk fats vary somewhat according to the general type of diet, the seasonal change from pasture to indoor feeding, the age of the animal, etc. Such variations are, in fact, chiefly connected with differences in the proportions of the unsaturated acids, which are mainly compensated by corresponding alterations in those of the stearic, and of the butyric and other lower saturated acids. The amounts of fully saturated components and of di-" oleo "-monosaturated glycerides are almost the only markedly variable features in the glyceride structure of butter fats, since this depends upon the relative amounts of saturated and unsaturated acids in the whole fat. Thus when the factor due to variable unsaturation (the varying fully saturated glyceride content) has been taken into account, close similarities are revealed in the respective fully saturated and non-fully saturated components of the butters, irrespective of the locality of their origin, seasonal or age conditions, etc.

The fat (EC) from cows whose diet had included a certain amount of coconut oil cake contained, as a whole, less oleic and linoleic acid than normal and somewhat more lauric and myristic acids. In its fully saturated components, however, the relative differences are more sharply defined : the lauric acid molar content (Table 91A (iii)) is 11 (instead of about 5–6) and the myristic acid molar content is 20 (against 15–17). Since dilauromyristin is a major component of coconut oil (*cf.* Chapter VI, p. 257), these figures suggest that to some extent this glyceride has passed through directly into the milk fat.

Whilst ingestion of the relatively highly saturated coconut fat led to variation from the normal in the character of the fully saturated components of butter fat EC, the diet including soya bean oil (nearly all of which consists of unsaturated glycerides) caused differences from the normal which are for the most part confined to the non-fully saturated glycerides in butter fat ES. In the latter case, however, the observed differences do not involve any increase in the proportion of linoleic acid (the major component of soya bean oil) but are confined for the most part to augmentation of the butyric-lauric acid group; thus suggesting that the latter might, in part, be metabolic products from the oleic or linoleic glycerides of soya bean oil which appear in the mixed saturated-unsaturated glycerides of the milk fat.

Indian camel, buffalo, sheep, and goat milk fats. The glyceride structure of the milk fats of the Indian camel, sheep, and goat have been studied by Dhingra,[38] and that of the Indian buffalo by Bhattacharya and Hilditch,[37] and by Achaya and Banerjee,[48b] on the same lines as those of the cow milk fats which have been considered above. The chief numerical results of the investigations are summarised in Table 93.

TABLE 93. *GLYCERIDE STRUCTURE OF INDIAN CAMEL, BUFFALO, SHEEP, AND GOAT MILK FATS*

(i) *Component Fatty Acids of the whole Fats* (*Molar Percentages*)

	Camel[38]		Buffalo		Sheep[38]	Goat[38]
		I[37]	II[48b]	III[48b]		
Butyric acid	5·9	10·9	15·4	11·5	8·4	7·6
n-Hexanoic acid	1·9	2·8	1·1	—	5·4	4·5
n-Octanoic „	1·1	1·5	1·4	0·1	5·8	6·2
n-Decanoic „	2·1	2·4	1·4	0·5	10·1	11·1
Lauric „	5·7	3·3	1·9	0·8	6·0	5·1
Myristic „	7·9	10·5	9·2	4·8	11·8	11·2
Palmitic „	28·3	28·7	31·9	25·1	20·4	21·5
Stearic „	9·7	9·3	12·5	19·0	5·4	7·3
Arachidic „	—	0·7	0·1	1·1	1·3	0·1
Oleic „	34·1	27·7	23·9*	36·1*	22·2	24·2
Octadecadienoic acid	3·3	2·2	1·2	1·0	3·2	1·2

* Includes minor accounts of hexadecenoic and unsaturated C_{20} acids.

(ii) *Fully Saturated Glycerides present in the whole Fats*

	Camel	Buffalo I	Buffalo II	Buffalo III	Sheep	Goat
Whole Fats:						
Iodine value	40·8	33·5	27·4	37·0	32·1	28·8
Total saturated acid content (per cent. mol.).	62·6	70·1	74·9	62·9		
Fully saturated glycerides:						
per cent. (wt.)	24·2	32·3	40·1	22·1	33·7	36·3
per cent. (mol.)	25·6	34·3	41·7	24·3	36·8	39·3
Mols. saturated acid per mol. unsaturated acid in non-fully saturated part.	0·98	1·20	1·32	1·04	1·49	1·40

(iii) *Component Fatty Acids of the Fully Saturated Glycerides* (*Molar Percentages*)

	Camel	Buffalo I	Buffalo II	Buffalo III	Sheep	Goat
Butyric acid	8·9	14·1			9·8	9·4
n-Hexanoic acid	2·1	5·0			8·2	7·2
n-Octanoic „	0·1	0·7			5·4	5·8
n-Decanoic „	2·8	1·6			10·8	14·2
Lauric „	2·6	4·4			14·1	8·2
Myristic „	18·9	9·2			15·9	12·7
Palmitic „	50·0	47·1			26·9	31·6
Stearic „	14·6	16·8			8·9	10·7
Arachidic „	—	1·1			—	0·2

(iv) *Probable General Composition of the Milk Fats* (*Molar Proportions*)

	Camel	Buffalo I	Buffalo II	Buffalo III	Sheep	Goat
Fully saturated	25	34	42	24	37	39
Mono-" oleo "-disaturated	37	42	41	40	50	46
Di-" oleo "-monosaturated	38	24	17	36	13	15

Buffalo I, pasture-fed; II, mainly pasture-fed; III, heavy cottonseed diet.

The camel and buffalo milk fat glycerides are, on the whole, very similar to those of the domestic cow. Butyric and *n*-hexanoic (caproic) acids are sub-normal in the whole camel milk fat, but this does not seem to be reflected in any departure from the normal in the general glyceride structure. The fully saturated glyceride content is slightly lower, for the proportion of saturated acids in the whole fat, than in the cow milk fats, as will be seen from Figs. 3 and 4 (pp. 297, 303); but the component acids of the fully saturated glycerides are, on the whole, not very different from those in cow milk fats. The buffalo milk fat [37] resembles a cow milk fat of the same mean unsaturation extremely closely, the only noticeable difference being a somewhat higher proportion than in the cow milk fats of palmitic and stearic acids in the fully saturated glyceride portion. The mainly pasture-fed buffalo milk fat II of Achaya and Banerjee[48b] is somewhat more saturated in nature than buffalo milk fat I, and contains notably more butyro-glycerides. The fat III, from a buffalo cow fed largely on cottonseed, is quite different and much more unsaturated, although its content of stearo-glycerides is at the same time increased; the effect of dietary fat on the character of the milk fat is evident in this instance (*cf.* this Chapter, p. 329).

Sheep and goat milk fats, on the other hand, seem to stand somewhat apart from cow or buffalo milk fats. Their relatively high contents of caprylic and capric acids received previous mention in Chapter III (p. 127). Their proportions of fully saturated glycerides are definitely lower than in the case of cow milk fats of corresponding mean unsaturation (Figs. 3 and 4, pp. 297, 303), whilst the component acids of the fully saturated portions contain, as is natural, much more caprylic, capric, and also lauric acid than those of the similar parts of cow milk fats, the palmitic and stearic acid contents being correspondingly below those of the latter. In the mixed saturated-unsaturated glycerides, however, the molar contents of myristic, palmitic, and stearic acids are very similar to those of the corresponding portions of cow butter fats, and the only difference is that, in the goat and sheep milk fats, there is about 10 per cent. (mols.) less of C_{18} unsaturated acids and 10 per cent. (mols.) more of the butyric-lauric acid group (the increase being mainly in capric and caprylic acids). The excess of capric and caprylic acids, as compared with cow butter fats, therefore appears to be almost wholly at the expense of oleic and, to a less extent, of palmitic acid. Sheep and goat milk fats are also remarkable for their extremely small proportions of di-unsaturated glycerides (ca. 15 per cent. of the fats); this however has less effect on their melting points than might at first be supposed, doubtless owing to the compensating influences of low contents of palmitic and stearic, with high butyric-lauric (especially caprylic and capric) acids.

More detailed study of a cow milk fat. The acetone crystallisation procedure was applied in 1940 to a typical English cow milk fat by Hilditch and S. Paul.[46] By systematic crystallisation from acetone at 0° and at 20° the fat was ultimately resolved into three fractions with the properties shown in Table 94A.

The data from the hydrogenated and crystallised fractions A, B and C, taken in conjunction with those for the fully saturated components present in each of these fractions, served to indicate the manner in which the unsaturated acids were united, with the remaining saturated acids, in mixed

TABLE 94A. *FRACTIONS (FROM ACETONE) OF COW MILK FAT*

FRACTIONS	A	B	C
Glycerides (per cent. wt.)	12·1	24·5	63·4
" (per cent. mol.)	11·4	24·2	64·4
Iodine value	21·5	36·8	55·2
Component acids (per cent. mol.):			
Butyric	—	8·1	13·0
Hexanoic	—	3·1	3·3
Octanoic	—	0·9	1·7
Decanoic	0·7	1·0	1·7
Lauric	2·3	1·7	2·0
Myristic	10·4	7·2	7·7
Palmitic	35·6	27·1	16·6
Stearic	26·7	15·8	7·2
Arachidic	1·4	1·0	0·3
Decenoic	Trace	0·1	0·2
Dodecenoic	0·1	0·1	0·2
Tetradecenoic	0·3	0·6	0·9
Hexadecenoic	1·1	1·7	2·2
Oleic	21·3	28·5	36·5
Octadecadienoic	0·1	2·7	4·9
Unsaturated C_{20-22}	—	0·4	1·6

The fully saturated glycerides and their component acids were determined in each fraction with the final results given in Table 94B, whilst portions of fractions B and C were also completely hydrogenated, after which these were further resolved by crystallisation from acetone and from ether, and the component acids of each sub-fraction determined.

TABLE 94B. *FULLY SATURATED GLYCERIDES PRESENT IN FRACTIONS A, B, AND C OF THE COW MILK FAT*

	A	B	C
Fully saturated glyceride content (per cent. mol.)	45·3	24·6	11·8
Component acids (per cent. mol.):			
Butyric	—	16·0	20·4
Hexanoic	—	7·1	3·4
Octanoic	—	3·9	7·0
Decanoic	1·8	3·9	6·5
Lauric	5·7	3·7	6·7
Myristic	13·8	8·7	14·8
Palmitic	42·7	33·8	30·1
Stearic	35·0	22·8	11·1
Arachidic	1·0	0·1	—

saturated-unsaturated glycerides. The number of component acids present rendered it difficult, in the mixed parts of fractions B and C, to reach precise conclusions as to the component glycerides present ; the best that could be done was to consider a number of alternative possibilities (some of which could be rejected as unlikely or impossible on the grounds of comparative solubility, or for other reasons). A number of possibilities remained for each fraction which, when the increments from the latter were assembled, led to the component glyceride data given in Table 94C, which must however be considered as relative and illustrative rather than absolute. Nevertheless these figures define, much more completely than has previously been possible, both the nature of the chief mixed glycerides present in cow milk fat and their general proportions.

The figures in Table 94C show that the most abundant glycerides in this butter fat (22–30 per cent. of the fat) contained one of the lower fatty acids

TABLE 94c. *COMPONENT ACIDS AND GLYCERIDES OF THE COW MILK FAT (PER CENT. MOL.)*

Component Acids	
Butyric	10·2
Hexanoic	2·5
Octanoic	1·3
Decanoic	1·5
Lauric	3·3
Myristic	8·6
Palmitic	21·1
Stearic	9·9
Arachidic	0·7
Decenoic	0·2
Dodecenoic	0·2
Tetradecenoic	0·9
Hexadecenoic	2·8
Oleic	31·4
Octadecadienoic	4·9
Unsaturated C_{20-22}	0·5

Component Glycerides	
Fully saturated (19 per cent.):	
Di-C_{4-14}-monopalmitin	6–7
Di-C_{4-14}-monostearin	1
Mono-C_{4-14}-dipalmitin	<1
Mono-C_{4-14}-palmitostearin	9
Dipalmitostearin	1–2
Palmitodistearin	<1
Mono-unsaturated (56–59 per cent.)	
" Oleo "-di-C_{4-14}	3–9
" Oleo "-C_{4-14}-palmitin	22–30
" Oleo "-C_{4-14}-stearin	6–12
" Oleo "-dipalmitin	1–5
" Oleo "-palmitostearin	8–17
Di-unsaturated (15–25 per cent.):	
Mono-C_{4-14}-di-" olein "	0–10
Palmitodi-" olein "	4–18
Stearodi-" olein "	1–8
Tri-unsaturated (0–7 per cent.):	
Tri-" olein "	0–7

(from butyric to myristic) in union with one palmitic and one oleic group as triglycerides. Nearly 40 per cent. of the fat was made up of four other groups of glycerides, these being (in probably decreasing order of magnitude) oleopalmitostearins, palmitodioleins, oleo-mono-C_{4-14}-stearins, mono-C_{4-14}-di-oleins ; the remaining 30–35 per cent. of the fat included about ten minor component mixed glycerides. The fully saturated glycerides (19 per cent. of the fat) consisted largely of mono-C_{4-14}-palmitostearins and di-C_{4-14}-monopalmitins. No indication whatever was obtained of the presence of tributyrin or, indeed, of any other simple triglyceride ; tri-unsaturated glycerides, if present at all, did not amount to more than 7 per cent. of the fat and were almost certainly mixed glycerides of oleic with another unsaturated acid (probably mainly octadecadieno-dioleins).

The cow milk fat component acids included 40·9 per cent. total unsaturated (31·4 per cent. oleic) and 21·1 per cent. palmitic acid. Unsaturated acids were present in 81 per cent. of the triglyceride molecules (once in 56–59 per cent., twice in 25–15 per cent., and three times (tri-unsaturated) in 0–7 per cent. of the fat) ; palmitic acid was present in about 70 per cent. of the triglyceride molecules (about 65 per cent. containing one palmitic group, and about 5 per cent. containing two palmitic acid groups).

It is interesting to compare these figures with those for the English heifer depot fat studied by Hilditch and Paul.[18a] The depot fat component acids contained 41·3 per cent. total unsaturated (37·1 per cent. oleic) and 32·2 per cent. palmitic acid. Unsaturated acids were present in 83 per cent. of the triglyceride molecules (once in 49 per cent. and twice in 34 per cent. of the fat) ; palmitic acid was present in about 83 per cent. of the triglyceride molecules (probably about 70 per cent. containing one palmitic group, and about 13 per cent. containing two palmitic acid groups).*

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* In the depot fat analysis, the minor component myristic acid was grouped with palmitic, whereas in the milk fat analysis it is placed with the lower saturated acids in the C_{4-14} group ; this renders a precise comparison difficult, but the depot fat figures have been approximately adjusted to allow for this difference.

Allowing for the increased proportion of palmitic acid in the depot fat, it will be seen that the general distribution of both the palmitic and the unsaturated (mainly oleic) acids throughout the butter glycerides is very similar to that in the depot fat. The general picture of the cow milk fat glycerides therefore remains that of a mixture of mixed triglycerides similar in many respects to that in the corresponding depot fat, except that the stearo-glycerides of the latter are largely replaced in butter by acyl groups of the characteristic lower fatty acids of the milk fat. To this extent the above detailed examination of a cow milk fat supports the view that the stearic groups of the depot fat and the lower saturated fatty acid (and minor lower Δ^9-mono-ethenoid acids) of the milk fat may well be derived from preformed oleo- (or octadecadieno-) glycerides; it does not, of course, provide any proof of the correctness of the hypothesis, but any alternative hypothesis must take into equal account the structural features of the milk fat glycerides which have now been demonstrated.

Human milk fat. A study of the component glycerides of human milk fat was published in 1944 by Hilditch and Meara.[46] The component acids of the fat (*cf.* Chapter III, p. 129) were: decanoic 2·1, lauric 7·7, myristic 9·0, palmitic 23·6, stearic 6·5, arachidic 0·9, dodecenoic 0·3, tetradecenoic 0·8, hexadecenoic 5·4, oleic 33·2, octadecadienoic (mainly linoleic) 7·1, and unsaturated C_{20-22} 3·4 per cent. (mol.). The fat was separated into four fractions after systematic crystallisation from acetone at temperatures varying between −25° and 0°; the proportions and component acids of the four fractions are shown in Table 95A.

TABLE 95A. *FRACTIONS (FROM ACETONE) OF HUMAN MILK FAT*

FRACTIONS	A	B	C	D
Glycerides (per cent. wt.)	23·7	18·7	21·3	36·3
,, (per cent. mol.)	24·0	19·0	21·3	35·7
Iodine value	26·4	36·6	57·4	95·9
Component acids (per cent. mol.):				
Decanoic	1·7	0·9	1·4	3·4
Lauric	6·6	7·9	6·7	9·0
Myristic	11·3	11·5	10·5	5·3
Palmitic	39·8	34·2	23·6	7·0
Stearic	14·0	9·5	5·1	0·5
Arachidic	2·0	0·9	1·0	—
Decenoic	—	—	Trace	0·1
Dodecenoic	0·1	0·1	0·7	0·3
Tetradecenoic	0·1	0·8	0·7	1·3
Hexadecenoic	4·0	2·6	4·4	8·3
Oleic	16·4	26·4	36·2	46·4
Octadecadienoic	1·1	2·7	7·0	13·8
Unsaturated C_{20-22}	2·9	2·5	2·7	4·6

Fully saturated glycerides were absent from fractions C and D, but present as follows in fractions A and B:—

A: 32·4 per cent. (mol.); component acids decanoic 1·5, lauric 13·3, myristic 22·8, palmitic 38·0, stearic 20·8, and arachidic 3·6 per cent. (mol.).

B: 7·2 per cent. (mol.); (taken as 50 per cent. palmitic, 25 per cent. each of lauric and myristic acids).

Owing to the less complex mixture of component acids and also to the employment of crystallisation from acetone below 0° (which evidently led to better separation of the more soluble glycerides in fractions C and D), the component glyceride data resulting from these calculations is of a more definite nature than was the case with the cow milk fat discussed above. The composition of the human milk fat was deduced as shown in Table 95B.

TABLE 95B. *COMPONENT GLYCERIDES OF THE HUMAN MILK FAT (PER CENT. MOL.)*

Fully saturated (9 per cent.):		*Mono-unsaturated* (40 per cent.):	
Di-C_{10-14}-monopalmitin	2	Mono-" unsatd."-C_{10-14}-palmitin	20
Mono-C_{10-14}-dipalmitin	2	Mono-" unsatd."-C_{10-14}-stearin	2
Mono-C_{10-14}-palmitostearin	5	Mono-" unsatd."-dipalmitin	4
		Mono-" unsatd."-palmitostearin	14
Di-unsaturated (43 per cent.):			
Mono-C_{10-14}-di-"unsatd."	24	*Tri-unsaturated* (8 per cent.):	
Palmitodi-" unsatd."	19	Probably mainly linoleodioleins	8

About half of the human milk fat consisted of glycerides in which at least two unsaturated acyl groups were present. In the di-unsaturated glycerides, about 24 per cent. (of the whole fat) contained, as saturated acyl group, myristic, lauric or decanoic acid, and about 19 per cent., palmitic acid. In addition, about 8 per cent. of the fat consisted of tri-unsaturated glycerides. Since there was 33 per cent. of oleic and 17 per cent. of minor unsaturated acids in the total fatty acids, it may be significant that there is just sufficient of the latter to account for these di- and tri-unsaturated glycerides being almost wholly constituted as mono-oleo-monosaturated glycerides and dioleo-glycerides respectively (the remaining acyl group in each class being contributed by one of the minor unsaturated acids—preponderantly linoleic). This is supported also by the distribution of linoleic acid in the different glyceride fractions revealed in Table 95A. If this be the case, oleic acid is almost the only unsaturated component of the mono-unsaturated-disaturated glycerides.

The lower saturated acids (myristic, lauric, decanoic) are seen to be distributed throughout the human milk fat with either (*a*) two unsaturated acyl groups, (*b*) oleic and palmitic, (*c*) palmitic and stearic, (*d*) oleic and stearic, or (*e*) one or two palmitic acid groups. Except for the two di-unsaturated groups already mentioned, the only major component glycerides of the fat are in fact 20 per cent. of mono-C_{10-14}-oleopalmitins and 14 per cent. of oleopalmito-stearins.

The amount of fully saturated glycerides (9 per cent.), although less than in cow milk fats, is much greater than the negligible amount which is found in fats containing about 50 per cent. each of saturated and unsaturated acids, when these follow the " even distribution " rule.

The above features are fundamentally similar to those subsisting in cow milk fats, where the range of lower saturated acids extends as far as butyric acid. This general similarity between the two milk fats is illustrated in Table 95C, which gives a summary of the total component acids of each fat, together with the proportions of glycerides containing (*a*) one lower saturated group, (*b*) two lower saturated groups, (*c*) one palmitic, and (*d*) two palmitic groups (i) in the human milk fat and (ii) in the cow milk fat (Hilditch and Paul[45]). Table 95C shows close similarity in the values for these respective groups of glycerides, having regard to the varying proportions of the acids concerned in the fats as a whole.

The palmitic glycerides are elaborated on similar lines in human and in cow milk fats, over 80 per cent. of the total palmitic acid in each case being present as monopalmito-glycerides. The lower saturated acids also occur predominantly in combination with two acyl groups of different character (palmitic, oleic, etc.), the proportion of glycerides containing two of these lower saturated groups being greater, however, in cow milk fat (in which

TABLE 95c. *COMPARATIVE GLYCERIDE STRUCTURE OF HUMAN AND COW MILK FATS*

Component acids (per cent. mol.):	HUMAN	COW
C_{14} and lower (saturated)	18·8	27·4
Palmitic	23·6	21·1
Stearic (+arachidic)	7·4	10·6
C_{16} and lower (mono-ethenoid)	6·5	4·1
Oleic	33·2	31·4
Octadecadienoic	7·1	4·9
Unsaturated C_{20-22}	3·4	0·5
Component glyceride groups (per cent. mol.):		
(*a*) Glycerides containing 1 C_{14} (or lower) saturated group	53	ca. 50
(*b*) „ „ 2 „ „ „ groups	2	ca. 15
(*c*) „ „ 1 palmitic group	60	ca. 65
(*d*) „ „ 2 „ groups	6	ca. 5

the lower acids form 27 per cent. of the total acids, as against 19 per cent. in the human milk fat).

These general resemblances in the glycerides of the two milk fats suggest that the mode of formation of the lower fatty acids may well be the same in both, but that the process proceeds much more extensively, and to a greater range of lower acids, in the production of cow milk fat than in that of human milk fat.

It is also interesting, in this connection, to compare the component acids of human milk fat with those of a female human depot fat as given by Cramer and Brown[47]: lauric 0·1, myristic 2·7, palmitic 24·0, stearic 8·4, tetradecenoic 0·2, hexadecenoic 5·0, oleic 46·9, octadecadienoic (mainly linoleic) 10·2 and unsaturated C_{20-22} acids 2·5 per cent. (wt.).

The resemblance to human milk fat in the palmitic acid content of the body fat is evident, and in both, linoleic acid contributes much of the octadecadienoic acids. The difference in the proportions of oleic acid in the two fats is roughly balanced by the increased proportions of C_{14}, C_{12} and C_{10} acids in the milk fat; moreover, just as the lower saturated acids are less abundant in human than in cow milk fat, so also there is less production of stearic acid in the human depot fat as compared with cow depot fat. In cow milk fat the production of short-chain acids is very prominent, but only traces of linoleic acid (the *cis-cis*-acid) are present, whilst in human milk fat the short-chain acids only extend to C_{10} (instead of C_4), and their amount is much less, but the fat still contains a significant proportion of linoleic glycerides. This arouses speculation as to whether linoleo-glycerides, as well as oleo-glycerides, may be precursors of the characteristic lower acyl-containing glycerides of milk fats (*cf.* pp. 306, 310).

It is not unnatural, in view of the large number of saturated acyl components present in milk fats, that it has so far not been possible to do more than deal with the component glycerides on general, instead of individual, lines. It can nevertheless at least be claimed that their investigation by the methods discussed has served to demonstrate their general composition and their close structural relationships to the corresponding depot fats. It can only be hoped that further research will in time permit at all events some of the more abundant individual components of this important group of natural fats to be more accurately defined.

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CHAPTER VIII

SOME ASPECTS OF THE BIOCHEMISTRY OF FATS

THE functions of fats in the living organism, and their importance in animal nutrition, have resulted in much investigation of problems such as their synthesis in the plant or animal, their assimilation and digestion in the animal system, the mechanism by which reserve fats may be utilised, and so on. The biochemistry of fats, indeed, covers a very wide and assiduously cultivated field, the adequate description of which requires a complete volume in itself. Such treatment, developed from the biochemical standpoint, has been given in several well-known monographs, some of which are referred to in the bibliography [1] attached to this chapter. It is thus superfluous (as well as impossible for reasons of space) to attempt to include in the present book a comprehensive survey of the biochemistry of natural fats. Moreover, as stressed at the outset (Chapter I, p. 1) the objective of this volume is to present as complete a statement as possible of the existing knowledge of the chemical constitution of natural fatty compounds, especially the glycerides. These materials are the end-products of a number of biochemical processes which are evidently complicated in character ; and it is in general a matter of some difficulty to interpret, from the chemical structure of end-products, the sequence of reactions which may have given rise to them. Nevertheless it seems certain that consideration of a number of the characteristic features concerning the component acids or glycerides found in the various groups of the vegetable and animal kingdoms can on occasion serve as a guide in assessing the soundness of hypotheses based upon more definitely biochemical investigations. In certain contingencies the evidence afforded by the chemical constitution of a natural fat may furnish decisive information as to whether a suggested mode of biosynthesis is in fact possible ; for instance, it might be clear that a suggested mechanism would involve the presence in the final product of component acids or glycerides which investigation has shown to be absent.

The discussion of fat biochemistry in this chapter is strictly limited to considerations of the nature suggested. Its object is to indicate how far, in the author's opinion, the existing data on the constitution of the lipids (which is still almost wholly confined, so far as fully detailed knowledge is concerned, to the glycerides) may have a useful bearing upon the study of their synthesis, assimilation, mobilisation, or transformation in the living organism. It will therefore be restricted to the following general topics :

(i) Synthesis of fatty compounds (*a*) in plants, (*b*) in animals ;
(ii) Possible mechanisms of the conversion of carbohydrates into fats ;
(iii) Assimilation of preformed fats by animals ;
(iv) Biochemical transformations of fats :
    (*a*) the mobilisation of reserve fat ;
    (*b*) rancidity and similar phenomena.

SOME ASPECTS OF THE BIOCHEMISTRY OF FATS

Biochemists will, it is believed, share the view that, in spite of the vast amount of careful experimental work which has been carried out, our knowledge of the development and utilisation of fats *in vivo* is still in many respects scanty, and often very uncertain. The problems are extremely difficult to study experimentally ; artificially designed tests, such as specific diets to animals, require the most careful interpretation in order to avoid erroneous conclusions ; and the isolation of intermediate metabolic products (which is an enormous aid in such studies) has rarely, if ever, been attained in connection with the synthesis or degradation of fats in the living organism. It is perhaps a consequence of the latter fact that several hypotheses have been put forward, attractive in themselves and plausibly accounting for some of the known characteristics of fats, but involving reactions or the production of intermediate products for which there appears to be, in some cases, no valid experimental evidence whatever. Moreover, no theory yet put forward takes any account of those specific features which have been shown by constitutive investigations to be outstanding characteristics of particular groups of natural fats.

The Biosynthesis of Fats in Plants

Any satisfactory explanation of the mechanism of fat-synthesis in the living plant must take into consideration the following, amongst other, definitely known facts :

(*a*) According to family, genus, or even species, the fatty acids combined in any one plant fat are specific in qualitative and quantitative composition.

(*b*) Speaking generally, there can be no doubt that the most abundant and widely distributed acid in all plant fats, seed or otherwise, is

Δ^{9}-oleic acid, $CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.CO_2H$;

with this are closely associated :

$\Delta^{9,12}$-linoleic acid, $CH_3.[CH_2]_4.CH{:}CH.CH_2.CH{:}CH.[CH_2]_7.CO_2H$,

and the saturated

palmitic acid, $CH_3.[CH_2]_{14}.CO_2H$,

all of which are found in practically all fats in amounts varying from very small to comparatively large (e.g. 30 or 40 per cent. or more of the total acids). Any complete theory of plant fat synthesis must account for the invariable appearance of these, their most characteristic components.

(*c*) The fats in all parts of all plants except the seed (endosperm or embryo) contain, almost always, only palmitic, oleic, and linoleic (linolenic) acids as major components ; many seed fats also contain only the same three or four major component acids, but many others (according to their families) contain specific major component acids (e.g. lauric, stearic, erucic, etc.) in large amounts.

(*d*) Except in the Palmæ, and perhaps one or two other families, it is rare, in seed fats, to find more than two saturated and two unsaturated acids as major components (*cf.* Tables 49–59 in Chapter IV). Whilst there are comparatively few families whose seed fats contain unsaturated acids other than those of the C_{18} series, the saturated acids which may be present in quantity range from lauric (C_{12}) to lignoceric (C_{24}), but, as stated, only one or two are usually present in any one instance. The range of molecular magnitude of the seed fat saturated acids is thus very wide, and demands considerable specificity in the synthetic mechanism whereby the seed fats are built up in different families.

(*e*) Finally, the mode of union of fatty acids into mixed glycerides must be considered, and it must be remembered that in seed fats and, probably to a large extent, in fruit-flesh fats the prevailing tendency is markedly in the direction of producing a mixture of triglycerides in which the fatty acids are distributed as evenly, i.e. as widely as possible amongst the glycerol molecules.

In the growing parts of plants, especially the leaves, it appears (*cf.* Chapter IV, p. 137) that glycerides and plant phosphatides are present in the cytoplasm in about equal, but small, proportions. The origin and functions of the leaf, etc., glycerides are at present uncertain (although if, as discussed below, fruit fats are derived from carbohydrates, it is likely that the same process may take place in the growing plant). It has, however, been believed for many years that the reserve fat stored in seeds or in the flesh of fruits is developed *in situ* and not translocated from the leaf or stem. This idea was based mainly on the fat present in olive trees: Rousille[2] was unable to detect any change in the fat content of the olive leaf during the ripening of the fruit, and Funaro[3] stated that the ether-soluble fat[*] from the leaves differed materially from the fruit-flesh olive oil. Even earlier, de Luca[4] had shown that olives could make fat after they were separated from the tree, and Pfeffer[5] had found that pæony seeds, when detached from the plant at an immature stage when they contained no fat, developed a certain amount of fat on being kept.

A more recent contribution to this subject by Burr and Miller,[6] which includes a full review of the earlier literature, describes a study of the respiratory quotients[†] of the castor bean during seed development and ripening, the results of which show that much fat is synthesised within the castor bean fruit; although a slow translocation of some fat from the leaf or other tissues is not excluded by the experiments of these workers, they clearly show that most of the seed fat is synthesised within the fruit itself.

It will be recalled that detailed figures for component acids, obtained by the modern methods, have demonstrated some similarity between leaf and fruit-coat fats, but have also established in very many instances the presence in seed fats of fatty acids which are absent from either the fruit-coat or leaf fats of the plants concerned.

The important question of the rapid and prominent development of fat in the ripening fruit has been the subject of many investigations, as a result of which it is usually accepted at present that there is adequate ground for believing that the fat is formed at the expense of carbohydrate. No satisfactory explanation of the mechanism of the conversion of carbohydrates into fats has yet been obtained, although various hypotheses of a more or less vague and unsatisfactory nature have been proposed (*cf.* pp. 358–367).

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[*] Many of the older observations, and unfortunately not a few of the more recent ones, appear to be based merely upon the saponification and iodine values, or even upon the weight alone, of the material extracted by ether from leaves, immature fruit, etc. In all cases but those of fully ripe seeds (and sometimes even there), ether also removes, of course, non-fatty matter, often in considerable amount; the value of the data, in the absence of further purification of the ether-soluble matter or at least of removal of non-fatty matter from the fatty acids obtained after hydrolysis, is therefore doubtful in many cases. To give trustworthy results, phosphatides should first be separated from the crude glycerides, and the fatty acids from the latter should be further purified from "unsaponifiable matter" before their amount and analytical values are recorded.

[†] The "respiratory quotient," or volume ratio of the carbon dioxide produced to the oxygen consumed, is to some extent a guide to the nature of the metabolic action. If carbohydrates are being completely oxidised, e.g.

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O,$$

the respiratory quotient is 1 : 1, whereas obviously for the complete oxidation of the long acyl chains of fats a greater proportion of oxygen would be required, so that the ratio of carbon dioxide formed to oxygen used would be less than unity. (For fats, it is about 0·7 : 1.)

On the other hand, if a more highly oxygenated substance is being converted into material of lower oxygen content, any oxygen intake will be less than the carbon dioxide output, and a respiratory quotient of more than 1 : 1 is observed. Leathes and Raper[1] state that "when satisfactory proof exists that carbohydrates are converted into fat . . . it is reasonable to assume that, when the R.Q. is higher than 1·0, then this reaction is the main one causing the high quotient. The reverse proposition, that when the quotient is lower than 0·7, fat is being converted into carbohydrate, cannot be so easily accepted."

We may refer, in the first place, to the morphological studies of Uhlmann[7] on the development of fat in fruits of various species. He found that in the earliest stages only starch and no fat was present; later the plasma commenced to contain fat in an extremely dispersed condition, no oil droplets being visible in the emulsion under the highest available magnification. As ripening proceeded, the starch granules became smaller and appeared to dissolve in the " oil-plasma "; some evidence of formation of sugar was also observed in most cases. Finally, as maturity approached, the oil commenced to separate from the plasma as a discontinuous phase in minute droplets, which ultimately became of considerable size and occupied the greater part of the cell under observation. This final, relatively rapid development of fatty oil occurred in the later phases of ripening.

On the chemical side, du Sablon[8] studied the relative proportions of starch, cane-sugar, glucose, and fat present in almonds and walnuts at various stages of ripening and found that general decrease in carbohydrate content accompanied the increase in fatty content. It may be pointed out that diminution in percentage content is not sufficient to prove the point, since the very great increase in the total weight of the seed during ripening might counterbalance a fall in percentage; the total amount of carbohydrate present at maturity might remain constant or even increase in spite of a drop in its percentage proportion. This does not appear likely to have occurred in du Sablon's results, however, since the glucose, at least, disappeared completely in both cases. Valée[9] confirmed du Sablon's results on almonds in 1903, and Ivanow[10a] in 1912 obtained similar data for a number of other seeds, and there is thus good reason to associate the production of fats with transformation of carbohydrates. Some of du Sablon's figures are appended below:

PERCENTAGE CONTENTS OF CARBOHYDRATES AND FAT IN ALMONDS DURING RIPENING (DU SABLON)

	JUNE 9	JULY 4	AUGUST 1	SEPTEMBER 1	OCTOBER 4
Glucose per cent.	6·0	4·2	0	0	0
Sucrose per cent.	6·7	4·9	2·8	2·6	2·5
Starch per cent.	21·6	14·1	6·2	5·4	5·3
Fat per cent.	2·0	10·0	37·0	44·0	46·0

PERCENTAGE CONTENTS OF CARBOHYDRATES AND FAT IN WALNUTS DURING RIPENING (DU SABLON)

	JULY 6	AUGUST 1	AUGUST 15	SEPTEMBER 1	OCTOBER 4
Glucose per cent.	7·6	2·4	0	0	0
Sucrose per cent.	0	0·5	0·6	0·8	1·6
Fat per cent.	3·0	16·0	49·0	52·0	62·0

A number of investigators have at different times studied the respiratory quotient, CO_2/O_2, of ripening oily fruits. Using excised seeds of poppy and of the castor bean, Godlewski[11] in 1882 found values for this quotient of 1·18 to 1·52 during ripening. The work of Gerber[12] (1897) on the ripening of olive fruits also affords some confirmation of the view that carbohydrates are the precursors of fats, for, in the stage of ripening when oil is being rapidly formed, the respiratory quotient rose to 1·51. This feature (which also holds for a short period in the case of fruits separated from the tree) is consistent with the transformation of carbohydrates into materials poorer in oxygen content. According to Gerber, the respiratory quotient is greater than unity only during the phase in which oil is being generated in quantity;

prior to this (in the soft green fruits), and also after maturity, the oxygen intake is greater than the output of carbon dioxide.

Gerber also observed that not only carbohydrate, but also protein, falls in concentration as oil is produced, as will be seen from the following figures :

OLIVE	AUGUST 30	SEPTEMBER 30
Protein per cent.	14·6	4·2
Fat per cent.	29·2	62·3

Seeds usually contain protein as well as fat, and it seems perhaps, at first sight, equally reasonable to postulate proteins or carbohydrates as possible progenitors of fats ; but the process of direct fatty acid synthesis from many proteins, the amino-acids in which contain branched carbon chains, would involve a fundamental alteration in the nature of the carbon skeleton. On the other hand, it is recognised that proteins can, in certain conditions, be converted into carbohydrates ; so that the conversion of proteins into fats may possibly take place *via* the intermediate stage of carbohydrate. If so, it becomes rather an academic question as to whether protein or carbohydrate is the fat-precursor.

Somewhat more definite knowledge is beginning to be gathered as to the later stages of fat-synthesis in the case of certain oil-bearing seeds. The earliest results in this part of the field were due to Ivanow,[10a] who in 1912 stated that rape, hemp, poppy, and flax seeds, in the early stages of development, contain oils in which considerable amounts of free fatty acids are present. In other words, formation of the free acids appears to precede the synthesis of the final mixed triglycerides, since at maturity the oils contain but little free fatty acid. Ivanow also observed that, in linseed oil (but not in the other three oils), the characteristic high iodine value is only attained in the final stages of ripening ; thus a crop, the ripe seeds of which contained oil of iodine value 175, yielded, seven weeks before complete maturity, immature seeds with an oil of iodine value 120.

These phenomena have been further studied by Ivanow and his colleagues and also by other workers. In the case of linseed oil, a very complete examination, carried out by Eyre and Fisher [13a] in 1915, was reported more fully by Eyre [13b] in 1931 ; a further investigation by Barker [14] confirmed the main features of Eyre's work. Eyre studied the rate of formation and the changes in the character of the oil in seeds of *Linum usitatissimum* and *L. caribrosum*, and showed that the acidic constituents of the fat are formed first. Whether glycerol is formed at the same time, or whether the formation of glycerol is delayed, is not clear. A remarkably rapid oil formation over a period of some 15 days was observed, and within this period an oil content of about 36 per cent., calculated on the dry weight of the seeds, was reached.

Changes in the nature of the oil continue after oil formation has ceased ; its unsaturated character, as measured by its iodine absorption, continues to increase. The development of fatty oil, and its changing unsaturation, is shown by the following figures :

DAYS AFTER FLOWERING	PER CENT. OIL (DRY SEEDS)	IODINE VALUE
10	2·5	114
14	15·1	119
17	31·1	127
23	37·0	143
28	36·9	170
35	36·8	180
51	36·3	190

Barker states that "it will be seen that the synthesis of the oil begins almost immediately after flowering and proceeds comparatively slowly during the first eleven days. At the end of that time a rapid accumulation of oil sets in, amounting to about 3 per cent. per day for some ten days, when, about 21 days from flowering time, the maximum oil content is reached." Beyond this point no appreciable increase in oil content occurred, but the iodine value of the oil increased, in the following 15–20 days, from about 130 to its normal value of 180–185.

The acidity of the oils in their earlier stages varied very much with the particular variety studied, as will be seen from the following data:

Days after Flowering	Per Cent. Fatty Acid (as Oleic Acid) in Oils from L. usitatissimum	L. caribrosum
14	4·3	42·0
17	—	11·8
20	2·1	7·2
23	1·1	3·6
28	—	1·7
32	0·3	—
66	0·3	0·4
76	0·2	—
84	—	0·1

Ivanow and Klokow [10b] subsequently stated that, in Moscow linseed, the linolenic acid content increases with maturity of the seed, whilst the oleic, and especially the linoleic, acid content diminishes. They suggest that fat-synthesis in the seed proceeds according to the scheme:

(i) Glucose→glycerol;
(ii) Glucose→saturated fatty acids→unsaturated fatty acids;
(iii) Fatty acids+glycerol→fat.

They identified acetaldehyde, propionic, hexanoic, octanoic, and decanoic acids in unripe linseed, sunflower seed, and mustard seed, and suggested that the lower acids are first formed in all seeds, but that, in cold climates, they are transformed into higher fatty acids as ripening proceeds.

The development of the cottonseed has been investigated on somewhat similar lines by American [15] and Russian [16] workers. The oil content of cottonseed increases regularly and very rapidly up to about 50 days, especially between the 20th and 30th days; up to 30 days, the increase in oil content is accompanied by that of gossypol, whilst sugar gradually decreases. Insoluble fibre increases rapidly, and water-soluble constituents decrease rapidly, up to the age of 35–40 days, after which both remain almost constant. The saponification values and the acid values of the oil decrease as the age of the seed increases, and the iodine value of the fatty acids increases up to 50 days, when it becomes constant. It appears that events in the ripening cottonseed follow a very similar course to those in the flax.

A similar study of fat formation in the ripening seed of a tropical plant was made by Sahasrabuddhe [17a] in the case of Niger seed (*Guizotia abyssinica*). The oil content of the seed is at a maximum 45 days after the flower opens, proteins appear in the seed 15 days after flowering and oil a few days later, whilst the amount of reducing sugars is greatest on about the 27th day and diminishes to zero by the time the oil formation is complete. The author states that the synthesis of lower fatty acids precedes that of the higher members and that hexoses and pentoses are more likely to be the source of the fat than polysaccharides. The observed phenomena agree exactly with those observed by Ivanow, Eyre, and others in the case of temperate plants, and the iodine value increases from 90 to 126 during the later stages of ripening of the seed. Humphries,[17b] studying the carbohydrate metabolism of the ripening cacao bean (*Theobroma cacao*), observed that after 87 days the fat content was only 1 per cent. of the dry weight of the bean, but in the next 12 days this increased to nearly 25 per cent., thereafter continuing more slowly to about 48 per cent. at maturity (170 days).

Rewald and Riede [18] made a somewhat wider study in the case of the soya bean plant, in that they have compared the proportions of protein, fat, and phosphatide in the growing part of the plant with that in the beans during the ripening period. At this time the amount of all three of these groups in the parts of the plant (including the seed pods or fruit coats) other than the beans decreases rapidly, but in the bean their proportions remain unchanged. The mean unsaturation of the bean oil exceeds that of the fat present in the pods, and the unsaturation of the bean oil increases during the final stages of ripening. In another leguminous plant, the white lupin, Neumann [19] has observed a similar state of affairs during ripening of the seed. The fat content increases from 2·5 to 11 per cent., with a decrease in acid value from 50 to 0, and an increase in iodine value from 106 to 114·5.

On the other hand, Bauer [20] examined oil from ripening sunflower seeds (grown from a single flower head); in this case the iodine value remained practically constant throughout (143–144), but variations in the thiocyanogen values indicated that the oleic acid content rose steadily during ripening, whilst those of the linoleic and saturated acids correspondingly decreased.

If, therefore, we may accept these studies as typical of the biosynthesis of the less saturated or " drying " oils, it is clear that the free fatty acids which are produced in the first instance are usually of an average order of unsaturation not far removed from that of oleic acid; lipoclastic esterification with glycerol apparently follows, frequently together with, or followed by, the production of glycerides of a more unsaturated nature than the fatty acids at first synthesised. Eyre considered that, whereas during the early stages a reducing system must obtain in order to lead to the formation of fatty acids from carbohydrates, the production of the more unsaturated fats in the later stages must be a quite separate process involving oxidation, i.e. desaturation, of the fatty acids already present. A dehydrogenation such as that suggested would however be extremely selective in character, for in linseed oil only the $\Delta^{9,12}$-linoleic and the $\Delta^{9,12,15}$-linolenic acids are present, and in cottonseed and other oils only $\Delta^{9,12}$-linoleic acids; moreover, the quantitative proportions of each of the component acids in the oil of the fully ripe seeds are invariably constant to within very narrow limits. Professor Chibnall [21] has however pointed out to the author that it is merely the interpretation of the data of Eyre, Ivanow, and others, on a *percentage* basis which necessitates the above desaturation hypothesis; and that, if the data are considered with reference to the *amount of fat per* 100 *seeds*, it is seen that the increase in unsaturation is due to *further synthesis* of highly unsaturated acids, and that there is no need to postulate that the fatty acids already formed undergo any further change. In studies of this kind it is clearly important to base conclusions upon a measure of the total amount of fat produced by a plant or animal; the percentage of fat in the dry seed has little significance except in its bearing upon the total weight of fat which has been synthesised. It is therefore more likely that the fat synthesised in the later stages is more unsaturated than that formed at the earlier period, than that any of the fat synthesised earlier subsequently undergoes desaturation.

It will be seen that, up to the present, these studies of the development of fat in ripening seeds have all been concerned with the frequently occurring category of seed fats in which the major component acids are confined to oleic, linoleic, and palmitic, with occasionally linolenic or stearic in addition. It would be extraordinarily interesting to make similar investigations in ripening fruits which give rise to large proportions of one or other of the more " specific " seed fatty acids—for example, rape or mustard seed (erucic as well as oleic and linoleic), seeds of the Palmæ (45–50 per cent. lauric acid) or Umbelliferæ (Δ^6- as well as Δ^9-octadecenoic acid), cacao butter, or other seeds whose fats are rich in stearic as well as oleic and palmitic acids, and many similar instances.

The delay in the synthesis of the triglycerides finally produced has not yet been completely explained, but is not difficult to understand. Possibly, as has been supposed, insufficient glycerol or lipase is present in the earlier stages, but it is more likely, as suggested by Terroine,[22] that the concentration of water in the seed cells in the early stages is too great to permit of complete synthesis of neutral fat. Remarkable features of the final synthesis into glycerides, if the process follows the general course indicated by the studies which have been mentioned, are (i) the completeness with which triglycerides are produced, with but little remaining free fatty acid and apparently no di- or mono-glycerides containing unesterified glycerol hydroxyl groups ; and (ii) the regularity of general structure (" even distribution " of fatty acids amongst the glycerol molecules) together with, according to the most recent indications, the production of triglycerides of selected configuration (e.g. β-oleodistearin, *cf.* Chapter VI, p. 271).

The Biosynthesis of Fats in Animals

The view originally held about a century ago that the reserve fat deposited in animal adipose tissue was derived entirely from fat taken as such in their diet was supplanted about 1850 by Liebig's opinion that animals must synthesise fats to a large extent. Liebig was led to this conclusion by consideration of the large amount of milk fat produced by lactating cows in relation to the fat in their diet, and of the fact, already beginning to be appreciated, that different kinds of animals feeding, for example, on similar pastures, laid down different types of reserve fat. Liebig considered that carbohydrates were the most probable source of animal fat, although Voit and Pettenkofer were later led to believe that proteins were the sole source of animal fat (a conclusion subsequently shown by Pflüger to be due to an error in computation). Clear proof that protein is a source of animal fat has, indeed, not yet been put forward ; but, in view of the fact that protein can, under certain conditions, undergo conversion into carbohydrate the question is in any case rather academic in character.

The proof that carbohydrates must be an important source of animal fat was first rigidly given by Lawes and Gilbert[23] in 1860–1866 in connection with the well-known Rothamsted experiments on the feeding of oxen, sheep, and pigs. The results were not always definite in the case of oxen and sheep, but were quite clear with pigs, as the following figures will demonstrate:

	Lb.
Protein in food	64·0
,, in animal	6·5
,, difference, *possibly* utilised for fat production	57·5
Fat in food	12·4
,, in animal	71·2
,, produced from other sources than fat in food	58·8
Carbon in fat produced (58·8 lb.)	45·3
,, in available protein (57·5 lb.), less carbon excreted as urea.	27·4
,, in fat which must have resulted from carbohydrate	17·9

Thus the minimum amount of fat which must have been derived from carbohydrate was about 26 lb., and this, of course, assumes that all unaccounted-for protein had also been transformed into fat—which is clearly improbable.

Similar quantitative evidence for the conversion of carbohydrate into animal fat was provided later by Rubner[24] for dogs and by Rosenfeld[25] for geese, whilst Morgulis and Pratt[26] showed that the formation of fat in the dog is accompanied by the high respiratory quotient necessary for this change.

A full examination was made by Hilditch, Lea, and Pedelty[27] of the component acids in the deposited fats of pigs reared on known diets (low in fat) under the direction of Dr. J. Hammond at the Animal Nutrition Station of the School of Agriculture, Cambridge; this investigation demonstrated on the one hand the extent to which fat had been synthesised in the animals, and on the other hand showed which of the fatty acids were produced by synthesis as distinct from assimilation—substantially only palmitic, oleic, and stearic. The component acids of the pig depot fats, and the diets given to the animals, in this experiment have been given in Chapter III (pp. 93–95 and Table 34A). From the data available at the Animal Nutrition Station on (*a*) the constituents of the diets and their fat contents, (*b*) the acids present in the small proportions of different fats in the diets,* and (*c*) the total weights and characteristics of fat present in the various depots (subcutaneous, perinephric and kidney, intermuscular, mesenteric, caul), together with the component acid data for selected fats from each animal, it was possible to construct a rough balance sheet showing (i) the total amount of each fatty acid ingested as fat by the animal, and (ii) the total amount of each fatty acid present as fat in the animals at slaughter. These figures are summarised in Table 96 (opposite page).

Irrespective of the particular diet concerned, these figures (with the exception of the pig fed to 16 weeks age on a restricted diet, in which very little fat was laid down) demonstrate that the amounts of saturated acids below myristic, linoleic, and unsaturated C_{20-22} acids in the deposited fats were less than those ingested as dietary fats, whereas the amounts of palmitic, stearic, and oleic acids in the body fats were greatly in excess of those ingested in the food fats; hexadecenoic acid, although small in quantity in any case, was present in greater quantity in the fats of the animals than in the fats they had ingested, whilst the amount of myristic acid in the depot fats was almost equal to that taken in the food fats.

Clearly, therefore, biosynthesis of fats containing palmitic, oleic, and stearic acid had occurred to a marked extent, whilst it seems certain that hexadecenoic acid and, very possibly, a little myristic acid was also synthesised as fat. On the other hand, it is equally clear that fats containing saturated acids of lower molecular weight than myristic acid were neither synthesised nor assimilated by the animal. (This accords with the previous observations [28] of workers on the body fats of rats and other animals.)

The amount of linoleic acid in the body fats was not more than, and usually definitely less than, half of that available in the form of ingested fat; this strongly suggests, although it does not form a conclusive proof, that, like the rat,[29] the pig is unable to synthesise linoleic acid and derives glycerides of this acid only by assimilation. The quantity of unsaturated C_{20-22} acids present as glycerides in the depots likewise falls short of that present in the diet (in this instance in the fish meal constituents); but the disparity is less pronounced than in the case of linoleic acid, and the possibility of some slight degree of synthesis of the acids of this group in the pig cannot be excluded. For the most part, however, they seem to be derived from the fish meal present in the feed of the animals.

Whilst it cannot, of course, be taken for granted that the increases in palmitic, stearic, and oleic acids represent the whole of the acids which have been synthesised, it is interesting to note that the weight ratios of the increases of palmitic to those of the two C_{18} acids (stearic and oleic) taken together in the five animals considered in the preceding table are 1 : 2·06, 1 : 1·86, 1 : 2·50, 1 : 2·17, and 1 : 1·90. The average ratio is 1 part of palmitic to 2·08 parts of C_{18} acids by weight, or 1 : 1·89 (molar). This is a somewhat striking confirmation, from a fresh angle, of the view put forward by the writer and his co-workers that palmitodioleins or their hydrogenated derivatives are the glycerides chiefly produced by synthesis in the pig and other animals for storage in the body tissues.

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* Previously published component acid analyses of the fats in question by the modern methods were utilised here.

TABLE 96. *COMPARISON OF ACIDS IN FAT INGESTED AND DEPOSITED BY PIGS*

(a) *Pigs at Different Planes of Nutrition to 200 lb. wt.*

PIG:	73 (HOG)			74 (GILT)			72 (HOG)			82 (GILT)		
PLANES OF NUTRITION.	LOW—HIGH			HIGH—HIGH			HIGH—LOW			LOW—LOW		
FATTY ACIDS (KG.)	FED	DEPOSITED	DIFFERENCE	FED	DEPOSITED	DIFFERENCE	FED	DEPOSITED	DIFFERENCE	FED	DEPOSITED	DIFFERENCE
Saturated												
Below C_{14}	0·11	Trace	−0·11	0·11	—	−0·11	0·12	Trace	−0·12	0·16	Trace	−0·16
Myristic	0·24	0·29	+0·05	0·26	0·24	−0·02	0·24	0·21	−0·03	0·27	0·15	−0·12
Palmitic	1·28	8·27	+6·99	1·53	6·92	+5·39	1·36	5·45	+4·09	1·28	4·00	+2·72
Stearic	0·25	3·99	+3·74	0·24	3·58	+3·34	0·20	2·99	+2·79	0·25	2·16	+1·91
Unsaturated												
C_{16} (and C_{14})	0·22	0·89	+0·67	0·22	0·72	+0·50	0·17	0·43	+0·26	0·22	0·31	+0·09
Oleic	3·24	13·87	+10·63	3·80	10·50	+6·70	3·27	10·69	+7·42	3·07	7·09	+4·02
Linoleic	3·30	1·48	−1·82	3·22	1·43	−1·79	2·44	1·07	−1·37	2·85	1·23	−1·62
C_{20-22}	0·87	0·74	−0·13	0·86	0·48	−0·38	0·66	0·53	−0·13	0·74	0·46	−0·28
	9·51	29·53	+20·02	10·24	23·87	+13·63	8·46	21·37	+12·91	8·84	15·40	+6·56

(b) *Pigs at Different Planes of Nutrition to 16 Weeks*

PIG:	138 (GILT)			139 (GILT)		
PLANES OF NUTRITION.	HIGH			LOW		
FATTY ACIDS (KG.)	FED	DEPOSITED	DIFFERENCE	FED	DEPOSITED	DIFFERENCE
Saturated						
Below C_{14}	0·08	Trace	−0·08	0·02	—	−0·02
Myristic	0·14	0·13	−0·01	0·04	0·01	−0·03
Palmitic	0·87	3·81	+2·94	0·32	0·15	−0·17
Stearic	0·07	1·14	+1·07	0·01	0·06	+0·05
Unsaturated						
C_{16} (and C_{14})	0·07	0·51	+0·44	0·01	0·03	+0·02
Oleic	1·97	6·48	+4·51	0·75	0·23	−0·52
Linoleic	0·73	0·38	−0·35	0·08	0·04	−0·04
C_{20-22}	0·21	0·25	+0·04	0·02	0·01	−0·01
	4·14	12·70	+8·56	1·25	0·53	−0·72

Similar studies of rat depot fats have been made by Longenecker,[29] who fed fasted animals on high carbohydrate and high protein diets, and found that the resulting body fat was very similar in each case :

Component Acids (Per cent. mol.)

DIET	SATURATED				UNSATURATED				
	C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	OLEIC	OCTA-DECA-DIENOIC	ARACHIDONIC
Carbohydrate	3·1	26·7	3·6	0·4	0·9	15·6	47·2	2·2	0·3
Protein	2·8	29·7	3·8	1·1	1·1	15·6	43·8	2·0	0·2

The total saturated acids amounted respectively to 33·8 and 37·4 per cent., with palmitic acid 26·7 and 29·7 per cent. The unsaturated acids are even more closely similar in proportion, with very low octadecadienoic acid contents ; an interesting feature is the proportion of hexadecenoic acid (15·6 per cent.), which is considerably higher than that observed in other experiments (*cf.* Chapter III, p. 79) where the rat diets were not wholly devoid of fat.

We may now pass on to the more general question of the different mixtures of fatty acids found in the fats of the various members of the animal kingdom. A complete review of this subject involves, of course, the greater part of the matter in Chapters II, III, and VII of this book, and it must be taken for granted that the reader has already made himself familiar with these details. Further, it is naturally most convenient to discuss many features of biochemical interest when specific groups of fats have been considered from the point of view of their component acids or glycerides. This has in fact been done at many points in the chapters mentioned, and there is no need to indulge in extensive repetition in the present discussion. All that will be attempted here is to recapitulate some of the outstanding features of component acid and glyceride composition of fats in the animal kingdom, with the object of stressing some of the ascertained facts which must be satisfactorily accounted for in any complete explanation of the processes whereby fats are synthesised in animals.

Marine animals. The characteristic and complex mixture of acids present in the glycerides of marine animals has been made abundantly clear by the data collected in Chapter II. The most significant feature, of course, is the high proportion of highly unsaturated C_{20} and C_{22} acids and of hexadecenoic acid—acids which are only present in very small proportions in the depot fats of land animals. Whilst the natural hexa- and tetradecenoic acids have a close structural resemblance to oleic acid in that all three contain the grouping $=CH.[CH_2]_7.COO-$, it must be borne in mind that all the existing evidence goes to show that the polyethenoid C_{20}, C_{22} (and also C_{18}) acids in these fats contain a quite different type of unsaturation. They are characterised by the presence of a number of groupings of the type $=CH.[CH_2]_2.CH=$, as well as $=CH.CH_2.CH=$, which appear to extend throughout the molecule, so that the chain of seven or more saturated $-CH_2-$ groups adjacent to the carboxyl group is not present ; unsaturation probably commences at the 4th or 5th carbon atom of the chain (counting the carboxyl carbon atom as 1). The difference in structure connotes difference in biosynthetic processes, or difference in the material which is metabolised into fat. It is of course frequently supposed that the larger fish or marine mammalia derive their fat entirely by assimilation—ultimately from diatoms or other plankton. No attempt seems yet to have been made to ascertain whether it is possible to frame an estimate as to whether, over a given period, there is sufficient fat produced as plankton fat to account for all the fat in all the larger marine animals. Assuming that this possibility were satisfactorily demonstrated, the interesting problems would remain as to why and how plankton metabolism leads to fat of this particular type, differing as it does from all fats found in the more developed flora and fauna.

In addition to the general composition of aquatic animal fats, which thus sets them apart from all other natural fats except those of aquatic flora, it must be remembered that, within this generalisation, a number of variations in the proportions (and in some cases the mean unsaturation) of the different homologous groups of component acids are discernible. These typical differences exist, broadly speaking, between the component acids of marine and freshwater fish fats, between the fats of Teleostid and Elasmobranch fish, and apparently between fish and whales of the North Atlantic and of the Southern oceans ; these and other instances of general or specific differences in the composition of aquatic animal fats have been discussed fully in Chapter II.

Moreover, a further complication arises in fish fats because in many species the liver acts as a depository of reserve fat in addition to its fat-producing rôle, whereas in many other species the reserve fat is diffused in the flesh, mesentery, head, etc., of the animal, the liver being relatively low in fat content, resembling in this respect the land animals rather than the first-mentioned type wherein the liver acts also as a fat store. The need for differentiating between the two groups has been stressed by Rapson *et al.*[30]

Land animals. The depot and liver lipids of the larger land animals have been dealt with in detail, from the standpoint of their component acids in Chapter III (pp. 85–110), and from that of their component glycerides in Chapter VII (pp. 297–305, 311–325). So far as the depot glycerides of the larger animals are concerned, the salient features are perhaps the relative constancy of the palmitic acid content at 30 (± 3) per cent., and of the C_{18} acids at 60–65 per cent. ; the approximate balance between stearic and oleic acid contents, the sum of which only varies relatively slightly ; the appearance of fully saturated glycerides (palmitostearins) in unusual proportions when, but not until, the stearic acid content of the fat rises above about 8–10 per cent. The observed glyceride components of stearic-rich depot fats can be accounted for by the hypothesis that preformed oleo-glycerides (mainly palmitodiolein) are converted to some extent by a hydrogenation process into the corresponding stearo-glycerides (e.g. oleopalmitostearin and palmitodistearin).

Liver fats. In contrast to most of the adipose tissues, the liver contains important quantities of phosphatides as well as glycerides, and the component acids of each of these groups differ from each other and also from the depot glycerides. The liver is usually regarded as the chief site of the synthesis, and also of the degradation, of fats in the animal organism. Definite evidence that the liver is concerned in fat metabolism was provided by the experiments of Hildesheim and Leathes [31] on the pig, dog, and rabbit. As in the case of vegetables, there is little or no clear evidence at present of the stages involved in the transformation of carbohydrate into fat.

The possible functions of animal phosphatides—those present in, for example, the muscles, heart, spleen, kidneys, and other organs, as well as those in the blood, the intestinal mucosa, and the liver—have been the object of much investigation and speculation. Those of the liver and intestines have been considered by many workers to represent, *inter alia*, an intermediate stage in the formation of triglycerides, but opinion on the point is not unanimous. Sinclair,[32a] for example, from observations of the influence of ingested fats of varying unsaturation on the phosphatides of the intestinal mucosa of the rat, found that these undergo a rapid turnover during fat absorption, but concluded that they did not function as intermediaries in glyceride metabolism. There are, however, other possible functions for the phosphatides : they may serve, by virtue of their physical property of miscibility with both aqueous and oil phases, as assistants in the permeation or transport of other compounds into or from the cells, or they may serve as an oxidation-reduction system, or they may be essential elements in the structure of certain cells. If the phosphatides of an organ are directly concerned as intermediaries in the metabolism of fatty acids in the organ, the component acids in the phosphatides would be expected to be those present in the fat ingested or synthesised by the animal.

In addition to the above-mentioned use by Sinclair [32a] of ingested fats of varying unsaturation, other means of "labelling" component acids in the dietary fats have been employed. "Iodised fats" (Artom *et al.*[33a]), elaidic glycerides (Sinclair [32b]), deuterium-containing fats (Cavanagh and Raper [34]), and the feeding of a mixture of olive oil and a solution of sodium phosphate containing the radio-active isotope of phosphorus (Artom *et al.*[33b]) have all been employed, and the results uniformly show rapid appearance of the "labelled" acids in the phosphatides of the liver, intestine, and frequently the blood plasma, but very slow appearance (or in some cases completely negative results) in phosphatides of the red cells of the blood, the muscles, heart, brain, and some other organs. Sinclair,[32c] in a concise statement on current views as to the functions of animal phosphatides, points out that the rapid turnover of fatty acids in the liver and intestinal phosphatides may mean that they represent an intermediary stage in glyceride re-synthesis or, equally well, that during fat absorption continuous synthesis of phosphatides goes on and that the products pass on into the blood. He adds that "in the case of the blood plasma, there appears to be no reason to doubt that part, at least, of the phospholipid consists of material which has been synthesised out of recently absorbed fatty acids and is being carried to the actively metabolising tissues when it is burned." The entire molecule of a liver or intestinal phosphatide is either being broken down and re-formed continuously, or is disappearing and is being replaced by synthesis.

Of the other functions suggested, there is some evidence [35] that muscle phosphatides may take part in oxidation-reduction processes as oxygen carriers, whilst there are many points which suggest that, in given cases, phosphatides form an essential part of the structure of specific cells (possibly in the cell membrane where they may assist in controlling the permeability of the latter to various compounds). The differences in the phosphatide contents of the muscles of wild and captive animals (Bloor *et al.*[36]) suggest that muscle phosphatide has a structural function, since it is more abundant in the (wild) animal of more active habit.

In the above paragraphs we have wandered rather more deeply than usual into some of the more strictly biochemical aspects of the phosphatides, and have departed somewhat from what were previously stated to be the limitations of this chapter. This has been intentional, and for two reasons. Firstly, to remind the reader once more of the present comparatively restricted nature of the more precise constitutional knowledge of lipids—extending only to the glycerides, a few of the waxes, and a very few phosphatides ; and secondly, to put in better perspective the fact that any single animal may well contain a large number of phosphatides differing in function and, very probably, in chemical constitution—the latter being still uncharted in detail except for a few liver phosphatides and those in other organs of one or two animals. We must now return to the more restricted problems which are the objective of this book.

The iodine values of liver fats are often (but not always) higher than those of the corresponding reserve fats, and it was long supposed that fatty acids may be desaturated in the liver. Desaturation must clearly operate during the breakdown of fats or during their reconversion into carbohydrate, if this takes place ; but it now seems unlikely that this process has any general application in the biosynthesis of unsaturated acids. Desaturation as the normal mode of synthesis of oleic and linoleic acids in the liver was considered by Leathes [37] to be supported by the circumstance that an isomeric form of oleic acid, Δ^{12}-octadecenoic acid, was reported by Hartley [38] to be present in the liver fat of the pig. This observation has since been proved by several workers [39] to have been mistaken, but its supposed importance as a support for the view that unsaturated acids are produced from saturated acids in the liver (presumably as indicating the probable origin of linoleic acid) does not in any case seem very clear. However this may be, the essential argument against desaturation as an intermediary stage in fat synthesis in the animal now rests on the specifically different nature of the acids concerned, and was pointed out at once by Klenk and Schoenebeck [40] as the result of their determinations of the component acids in ox liver phosphatides, glycerides, and depot glycerides : the highly unsaturated acids of ox liver fat consist of members of the C_{20} and C_{22} series, which clearly cannot result from desaturation of the reserve fat acids, which belong almost entirely to either the C_{16} or C_{18} series.

The general distribution of the component acids in the depot glycerides and the liver glycerides and phosphatides has now been shown in the cases of the ox, sheep, and pig to be characteristically different, and the table given in Chapter III (p. 110) dealing with this feature may be repeated here :

ACID	DEPOT GLYCERIDES	LIVER GLYCERIDES	LIVER PHOSPHATIDES
Palmitic	High	High	Lower
Stearic (variable)	High	Low	High
Hexadecenoic	Very low	Higher	Medium
C_{18} unsaturated (mainly oleic)	High	High	Lower
C_{20} and C_{22} (highly) unsaturated	Very low	Medium	High

Notwithstanding the larger amount of $C_{20\text{-}22}$ unsaturated acids in the liver phosphatides, stearic acid is actually more abundant in the liver phosphatides than in the glycerides, whilst there is more hexadecenoic acid in the liver glycerides than in the liver phosphatides. Such figures suggest, *prima facie*, no simple interconnection between the three classes of fats, but rather that each is constructed so as to contain a quite specific and different mixture of component acids. This does not help towards a clearer understanding of the inter-relationships of the three groups, it is true, but it should deter us from too ready acceptance of explanations which, though relatively simple, cannot in this case cover the facts disclosed by the chemical constitution of the fats in question.

Reserve fats. Although physiologists may not have reached a completely final decision upon the point, the consensus of opinion is that reserve fats are not synthesised in the cells of adipose tissue from carbohydrate, etc., conveyed to them by the blood stream, but that they receive the fat (either as such, or as fatty acids or soaps) from the latter. Consideration of all the facts now known seems to suggest, indeed, that the reserve fats are carried by the blood stream in the form of glycerides. It has already been pointed out that the close relationships between the glyceride structure of reserve fats from different animals or from different parts of the same animal appear to point to the production of these bodies by the same mechanism and, in any one animal, probably at one site. It is practically impossible to reconcile the production of reserve fats in the adipose tissue cells, either by transformation of phosphatides or by direct synthesis from fatty acids or soaps, with the particular component glycerides which they have been observed to contain.

At first sight it may appear equally impossible that the concentration of glycerides normally present in the blood stream should suffice as the source of adipose tissue fat, but a simple calculation will show that this is not so. From the data in such experiments as those quoted in this chapter it appears that the quantity of reserve fat deposited per day in a pig which is being fattened is of the order of 100–200 grams, or about 4–8 grams per hour The concentration of *glycerides*, as distinct from other fatty compounds, in the blood stream has not yet been given very accurately, but is probably of the order of 0·2–2 per cent. (according to circumstances).* As Leathes and Raper have pointed out,[41] in order to carry more fat from one site to another, the blood need not contain more ; it is a question of rate of transfer, not of concentration. In the case of the lactating cow, Kay *et al.*,[42a] followed by Maynard *et al.*,[42b] and by Shaw and Petersen,[42c] have shown, from the rate of flow of blood through the mammary gland and the glyceride content of the blood, that the amount of glycerides passing into the gland in the blood stream is sufficient to provide all the milk fat formed (other findings by these workers having pointed to the blood glycerides as the precursors of the milk glycerides).

From the comparative studies of the glyceride structure of animal depot fats referred to in Chapter VII (pp. 297–305) it may well be supposed that the primary phase of the glycerides which finally appear as reserve fat is that of a comparatively unsaturated mixture produced by lipolytic esterification of the mixed fatty acids formed initially by synthesis from carbohydrate, etc. These glycerides will usually contain about 25–30 mols. of palmitic and about 75–70 mols. of oleic (with diethenoid C_{18}) acids, and may be synthesised in the liver and pass thence into the blood stream. In those animals which produce reserve fats with important contents of stearic glycerides, however, a partial reduction of some of the oleic glycerides (after synthesis) may also be postulated before the fat mixture emerges into the blood stream from the intestines. Such a sequence of processes would be capable of yielding glyceride mixtures having the specific structures observed in lards, tallows, etc. The deposition of related fats differing in degree of saturation (stearo-glyceride contents) would, on this hypothesis, depend upon differentiated or selective absorption of the various glycerides in the blood stream by the cells of different adipose tissues.

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* For studies of the fatty compounds present in the blood of animals fed under various conditions, the papers of L. Lattes (*Arch. Exp. Path. and Pharm.*, 1911, **66**, 132) ; W. R. Bloor and co-workers (*J. Biol. Chem.*, 1914, **17**, 377 ; **19**, 1 ; 1915, **23**, 317 ; 1916, **25**, 577 ; 1917, **29**, 7 ; 1918, **36**, 49 ; 1922, **52**, 191) ; E. F. Terroine (*J. Physiol. Path. gen.*, 1914, **16**, 212 ; *Ann. Sci. Nat. Bot.*, 1920, (x), **2**, 1), and others may be consulted.

Much further experimental inquiry is still needed, however, before a definite conclusion as to the mechanism of animal reserve fat synthesis and deposition can be put forward with complete confidence.

The nature of depot glycerides in different animals depends, of course, on a number of other factors in addition to the basal diet from which the fat has been synthesised. Thus, in the group of body fats which contain little stearic acid (Chapter III, Tables 23, 28A, and 28B, pp. 71, 79), the nature of the unsaturated acids appears to vary according to the species, and probably also according to differences in life-habit, etc. Thus the body fats of the domestic fowl seem to contain a fair amount of linoleic acid, although this may be due to some extent to ingested fat. It is an old observation that, judged by average iodine values of the fats, wild animals produce a much more unsaturated reserve fat than those bred in captivity. Thus the iodine value of fat from the wild goose was 99·6 as compared with 67·0 for the fat from domestic geese [43]; and that of fat from rabbits was 101·1 (wild) and 64·4 (tame).[43] These differences might be due to the food, or to external conditions.

Relations between body temperature and the composition of reserve fats. An interesting feature of reserve fat composition is its connection with the site in which it is deposited. In the pig, it will be seen that the intestinal adipose tissue surrounding the kidney is distinctly more saturated than the inner layer of the back tissue fat, and this, in its turn, than the outermost layer (due, almost entirely, to the replacement of oleo-glycerides by stearo-glycerides in the more saturated fats). In the hen, on the contrary, the fats from the two external tissues, the neck and the abdominal layer, were found to be practically identical with the layer of fat on the inner surface of the mesenterium.

The usual explanation of these phenomena, and one which seems probable, is that they are mainly conditioned by the temperature of the tissues in which the fat is deposited. In the case of birds, whose skin is well protected from external temperature changes by their feathers, it is not therefore unnatural, on this hypothesis, to find that depot fat from different parts of the body, whether intestinal or outer tissues, is of much the same composition in all cases.

The differences in the composition of fat from the adipose tissues of the pig were first correlated with temperature by Henriques and Hansen [44] in 1901, who compared the setting points and iodine values of fats from various sites with the body temperatures in the case of a pig fed on barley with the following results:

	SOLIDIFYING POINT	IOD. VALUE			BODY TEMPERATURES
Outer back fat					
outermost	—	60·0	Back tissue	1 cm. deep	33·7°
inner layer	26·4°	57·1		2 ,, ,,	34·8°
Inner back fat					
outer layer	28·0°	51·8		3 ,, ,,	37·0°
innermost	27·7°	50·6		4 ,, ,,	39·0°
Perinephric fat	29·6°	47·7	Rectum		39·9°

They also kept three pigs from the same litter for two months, one at 30–35°, one at 0°, and one at 0° but covered with a sheepskin coat; the iodine values of the outermost layers of the back fats of the animals were, after this treatment, respectively 69·4, 72·3, and 67·0, thus supporting their hypothesis.

The composition of the inner layer of the pig back fats (i.e. beneath the "streak") was apparently more or less homogeneous in Henriques and Hansen's experiments, and this, as well as their general findings, was fully confirmed by detailed analyses by Dean and Hilditch [45] of the component acids of fat taken from five layers of the adipose tissue from the back of a sow fed on a non-fatty diet (see Chapter III, Table 33 (v), and p. 96).

It has been said [46] that "Fat to be of use as a source of energy in the body must be just fluid at the natural body temperature, and as a consequence the fat of cold-blooded animals (fish) is of very low melting point, while the fat of the sheep which has a high body temperature (104° F.) is of higher melting point than that of the bullock with a lower body temperature (101° F.)." Whilst it is clear that fats present in an animal (or plant) must be almost completely, if not wholly, liquid at the natural temperature of the organism, it does not necessarily follow that warm-blooded animals always produce fats of higher melting point and more saturated character than cold-blooded animals or plants which are indigenous to cool regions.

The instances of fats of fish, sheep, and bullock given in the quotation, for example, should be considered in conjunction with those of such animals as the rabbit (body temperature 103–104° F.) or the hen (104–108° F.). Whilst sheep fat contains only about 40 per cent. of unsaturated acids (mainly oleic), rabbit fat contains nearly 70 per cent., most of which is linoleic acid, with appreciable quantities of still less saturated acids. Again, hen fat contains about 70 per cent. of unsaturated (oleic and linoleic) acids, in spite of the high body temperature of the bird; this fat is, indeed, almost completely liquid at room temperature. Further, the rat, with a body temperature of 100° F. (lower than that of the rabbit) contains about the same high proportion of unsaturated acids, but these consist almost wholly of oleic acid: the more unsaturated linoleic acid, present in great quantity in rabbit fat, is almost absent from that of the rat.

It has also been usual to connect the liquid, very highly unsaturated fats of fish with their low body temperature; yet marine mammals such as the whale, dugong (102–104° F.) or porpoise (96–98·6° F.) have body temperatures of the same order as those of land animals, whereas their fats are very closely similar in composition to the fish oils, and include the same series of highly unsaturated acids.

No wide generalisation can therefore safely be drawn between temperature of the organism and the composition of its fat. Fats which are solid at the normal temperature of plants or animals are obviously incompatible with their conditions of life, but, of animals and plants which exist under relatively warm conditions, some utilise fats of a relatively saturated (solid) character, but others resemble the cold-blooded animals and temperate plants in having fats of a more unsaturated and liquid type. Body temperature clearly plays a part in some instances, but this is often less clearly defined than that conditioned by species or other biological factor.

Milk fats. The component acids and glycerides of milk fats were discussed in Chapters III (pp. 112–130) and VII (pp. 306–310, 326–336), and at the same time their relationships to the depot fats were pointed out. Their characteristic composition can be explained on the hypothesis that the same comparatively unsaturated mixture of glycerides (with 25–30 mols. of palmitic to 75–70 mols. of oleic acid, which, on the one hand, may undergo partial hydrogenation before it appears as depot fat, e.g. in the ox or sheep) is transformed within the mammary gland, oleo-glycerides being converted into those of the shorter-chain, mainly saturated acids. Evidence from several angles in support of this hypothesis has been dealt with in the two previous chapters already mentioned (see, especially, Chapter VII, pp. 306–310), to which the reader is referred. Here it need only be repeated that the evidence in favour of blood glycerides being direct precursors of milk glycerides is almost complete, but that, although the mechanism of production of the latter postulated by the above hypothesis is consistent with the points brought out by the determination of the constitution of milk fat glycerides, there is still no direct experimental evidence as to what actually goes on.

To sum up the present section of this chapter, it may be said that at present there seem to be good reasons for the belief that fats are manufactured from carbohydrate, etc., in one central site of the animal body, probably the liver. The fats produced pass into the blood stream and are thence absorbed selectively as required by the cells of the various fat depots. Quite probably, of course, at different stages of the life cycle (for example, during the gestatory and lactation periods of the female mammal) modified types of blood fat may be produced by the synthetic processes; it is also becoming apparent that, with advancing age, the general character of the reserve fats of an animal alters in some degree. On the basis of a single site of fat biosynthesis from carbohydrate, etc., in the animal, the general structural similarities which have recently been shown to exist between fats so apparently different in composition as milk fats and tallows cannot be regarded as unexpected; indeed, the structural likenesses which have been brought to light may rather be regarded as confirmatory evidence of a single centre of fat synthesis in the animal.

Possible Mechanisms of the Conversion of Carbohydrates into Fats

At this point, since we have seen that there is abundant evidence that carbohydrates are at all events the main source from which fats are produced by plants and animals, it is necessary to review the hypotheses which have been advanced from time to time to account for this transformation. The matter will perhaps ultimately prove more difficult to explain in the case of plant fats than of animal fats, for there is less qualitative difference, for example, between the reserve fats of many terrestrial animals (and possibly birds), or between the liver oils of most fishes, than there is between the seed fats of different botanical families. Put in another form, the problem is not merely to give a reasonable explanation of how glucose or fructose or starch can be chemically converted into a general mixture of fatty acids or glycerides ; we have also to explain, for example, why the sugars present in the growing endosperm of Palmæ species yield the characteristic Palmæ kernel fatty acids (50 per cent. lauric, 20 per cent. myristic, etc.), while those in the cotton seed lead to a fat with about 25 per cent. each of palmitic and oleic and 50 per cent. of linoleic acid, those in the nutmeg produce 75–80 per cent. of myristic acid, in the castor seed 80 per cent. of ricinoleic acid, in seeds of certain *Aleurites* 80 per cent. of elæostearic acid, in seeds of the Cruciferæ 30–40 per cent. of erucic acid, in those of the Umbelliferæ varying amounts of petroselinic acid, and so on. Together with this, we must remember that, in a great number of other plant families, the main component acids of plant fats are large quantities of oleic and/or linoleic acid with (usually) less palmitic acid.

Indeed, in the vast majority of natural fats the most abundant component is oleic acid ; and, if we include with oleic the structurally closely related linoleic, linolenic, and elæostearic acids, a still larger proportion of the fatty acids present in nature fall into this one group. Logically, therefore, one would have considered that explanation should have been sought for the production from carbohydrates of the most characteristic structure found in all natural fats :

$$CH_3.[CH_2]_7.CH{=}CH.[CH_2]_7.COO-$$

In fact, this has never been seriously considered. Instead, attention has been concentrated on another feature of natural fats—the almost exclusive occurrence of straight-chain fatty acids containing an even number of carbon atoms in the molecule. This obviously has an important meaning in connection with the biosynthesis of fats, but it may prove somewhat unfortunate that attention has been diverted so much from the equally fundamental problem of accounting for the synthesis of the most abundant component of all, oleic or Δ^9-octadecenoic acid. However that may be, much consideration has been given to the possibility that carbohydrates are first broken down to a two-carbon unit (e.g. acetaldehyde), which serves as a basis for re-assemblage into fatty acid chains containing even numbers of carbon atoms.

Parallel with the development of various hypothetical sequences of reactions whereby higher fatty acids might result from aldol or other condensations of acetaldehyde, attempts have been made to ascertain whether fats can be produced by living organisms from this compound or related substances such as pyruvic acid, and a brief summary of these may preface discussion of the more theoretical hypotheses.

Enzyme syntheses of fatty acids and fats. In 1925 Haehn and Kinttof[47] published the results of some interesting studies of fat synthesis by the yeast mould *Endomyces vernalis*. They first showed that glucose was fermented by the mould with production of fatty matter (30–37 per cent. of the weight of glucose fed) which contained 23–30 per cent. of free acids (reckoned as oleic), and had mean equivalents of 235–245 and iodine values of 64·6–105·2. (It will be noted that these characteristics indicate that either considerable proportions of lower saturated acids accompanied C_{18} unsaturated (oleic and linoleic) acids, or that unsaturated acids of lower molecular weight than the C_{18} group were also present in quantity. In any case, the recorded equivalents are extremely low by comparison with other mould fats the component acids of which have been studied in more detail, *cf.* Chapter IV, p. 135.) They then made other experiments in which dilute (1–4 per cent.) aqueous solutions of pyruvic or lactic acids, acetaldehyde, aldol, alcohol, and glycerol were used as nutrients, and in each case observed considerably increased formation of fat as compared with the respective control experiments:

	Percentage of Fat (as Fatty Acid) in the Yeast Moulds		
Nutrient Added	Added Nutrient	Control	Increase
Pyruvic acid	11·2	3·3	7·9
Lactic acid	10·0	2·7	7·3
Acetaldehyde	8·3	2·8	5·5
Aldol	24·3	6·8	17·5
Ethyl alcohol	28·1	3·0	25·1
Glycerol	16·8	3·0	13·8

At about the same time Smedley-MacLean and Hoffert[48] concluded, from studies of fat and carbohydrate production in growing yeast, that acetaldehyde is first condensed to hexose, which is either converted into storage carbohydrate or directly condensed into higher fatty acids without passing through a fatty aldehyde stage, and probably by a direct linking of the hexose molecules.

In 1929 Barber[49] showed that *Penicillium* cultures grown in solutions of glucose, sucrose, xylose, or glycerol produce fat to about the same extent and containing the same type of fatty acids (20–30 per cent. saturated (mean mol. wt. 270–290) and 80–70 per cent. of unsaturated, iod. val. about 110–120). The amount of fat obtained, however, was very small in relation to the total sugar present, and it appears uncertain whether the experiments conclusively show any direct connection between the carbohydrate in the medium and the resulting *Penicillium* fats:

	Medium Sugar		*Penicillium* Growth Finally Produced					
					Neutral Fat		Mixed Fatty Acids	
	c.c.	g.	g. (Dry)	Free Fatty Acid g.	g.	Per Cent. Sterols	M.M.W.	Iod. Val.
Glucose	4,000	200	31	0·83	4·92	2·5	286	88
Cane sugar	3,500	175	26	0·18	2·03	13·0	291	80
Xylose	2,000	60	13	0·34	1·63	8·0	280	91
Glycerol	5,500	550	30	0·22	3·21	4·5	284	86

In 1938, following the chemical syntheses (referred to below) of higher polyene aldehydes and reduction of the latter to fatty acids by Kuhn and others, Reichel and Schmid [60] repeated and extended Haehn and Kinttof's observations with *Endomyces vernalis*. They found that glucose, fructose, or cane sugar were converted to the extent of about 25 per cent. into fatty matter, the originally fat-free cultures containing at the end of the tests 7–12 per cent. of neutral fat and 5–8 per cent. of free higher fatty acids; fructose was an exceptionally good source of fat. They also found that, whilst higher saturated aldehydes (e.g. octyl or decyl aldehydes) were merely oxidised to acids of the same carbon content, polyene aldehydes, such as hexadienal $CH_3.[CH{:}CH]_2.CHO$, or octatrienal $CH_3.[CH{:}CH]_3.CHO$, were converted into higher fatty acids. Reichel and Schmid suggest that three molecules of hexadienal yield $CH_3.[CH{:}CH]_{16}.CHO$, which is oxidised to the corresponding acid and also reduced, firstly to oleic acid, and possibly further to stearic acid; whilst condensation of two molecules of octatrienal similarly leads to palmitic acid. Although they could not repeat Haehn and Kinttof's result with pure glycerol, they found that mixtures of glycerol with either pyruvic acid, acetaldehyde, crotonaldehyde, hexadienal, or octadienal yielded the mixture of fatty acid and fats. Without giving analytical characteristics, they state that possibly the components of the products are linoleic, oleic, stearic, and palmitic acids and conclude with the statement—possibly somewhat premature or, at least, comprehensive—that their further experiments will completely elucidate the mechanism of fat synthesis. Interesting and valuable as Reichel and Schmid's demonstration is that Kuhn's polyene aldehydes are also utilisable by enzymes as material for higher fatty acid synthesis, their work may well be regarded as pioneering rather than final, and no doubt other microbiologists will be attracted to this problem; in which case more progress will ensue if the nature of the component acids of the synthesised fat is more closely examined than in any of the studies mentioned in the preceding paragraphs.

Theoretically possible mechanisms of fat synthesis from carbohydrates. We will now return to the consideration of various mechanisms which have been put forward as tentative possibilities in the biosynthesis of higher fatty acids. First of all we may deal with the suggestions which are obviously influenced by the even number of carbon atoms present in practically all acids of natural fats. There are two main variants of this hypothesis.

Nencki [51a] suggested as long ago as 1878 that acetaldehyde might be produced from lactic acid and then condense to give fatty acids; Magnus-Levy [51b] and Leathes [51c] indicated at a later period the manner in which this might occur; for example:

$$\begin{array}{ccc} CH_3.CHO+CH_3.CHO & & \\ \text{Acetaldehyde} & & \\ \downarrow & & \\ CH_3.CH(OH).CH_2.CHO & \xrightarrow[\text{and reduction)}]{\text{(Simultaneous oxidation}} & CH_3.CH_2.CH_2.COOH \\ \text{Aldol} & & \text{Butyric acid} \end{array}$$

Repeated condensations of aldol with itself or with acetaldehyde would result in similar building up of any of the higher normal saturated acids of the general formula $C_{2n}H_{4n}O_2$. The possibility that such condensations, higher in the series, would lead to branched-chain products was shown to be unlikely by the experiments of Raper[52] and of Smedley[53a] on the autocondensation respectively of aldol and of crotonaldehyde.

Lubrzynska and Smedley[53b, 53c] advanced, as an alternative, the suggestion that acetaldehyde or its condensation products condensed with a molecule of pyruvic acid to yield derivatives which by further change would result in the production of saturated acids :

$$\begin{gathered}CH_3.CHO+CH_3.CO.COOH \rightarrow CH_3.CH{:}CH.CO.COOH+H_2O\\ CH_3.CH{:}CH.CO.COOH \rightarrow CH_3.CH{:}CH.CHO+CO_2\\ CH_3.CH{:}CH.CHO+CH_3.CO.COOH \rightarrow CH_3.CH{:}CH.CH{:}CH.CO.COOH+H_2O\\ CH_3.CH{:}CH.CH{:}CH.CO.COOH \rightarrow CH_3.CH{:}CH.CH{:}CH.CHO+CO_2\\ CH_3.CH{:}CH.CH{:}CH.CHO+4H+O \rightarrow CH_3.[CH_2]_4.COOH;\ \text{etc.}\end{gathered}$$

The intervention of pyruvic acid (produced during the breakdown of glucose by enzymes) in the conversion of hexoses to fatty acids is made almost certain by the discovery by McHenry *et al.*[54] that vitamin B_1 is necessary for the synthesis of fats in the animal. Vitamin B_1 (aneurin pyrophosphate) is known to be the co-enzyme (" co-carboxylase ") necessary for the enzyme carboxylase to exert its decarboxylating action. In other words, decarboxylation of pyruvic acid may be almost certainly an essential step in the synthesis *in vivo* of fatty acids from sugars, but this still leaves open the question of whether the acid itself, or acetaldehyde produced from it by loss of carbon dioxide, undergoes condensation.

On the other hand, Boxer and Stetten,[55] confirming a supply of aneurin as a *necessary but not sufficient* condition of fat-synthesis, ascribe the effect of lack of vitamin B_1 to loss of appetite, and not to its specific effect in the syntheses.

Smedley-Maclean[1] (" The Metabolism of Fat," p. 26) says : " It may be that pyruvic molecules combine directly to form the fatty acid chains, decarboxylation occurring at the moment of combination, but the possibility that acetaldehyde may be first formed from pyruvic acid, and that this may be the material which undergoes successive condensations to unsaturated aldehydes, cannot be excluded. The formation of fat from the C_2 compounds, ethyl alcohol and acetic acid, by yeast and other lower organisms is perhaps more readily explained if acetaldehyde be the unit of condensation. At present we must await further evidence as to the paths by which alcohol and acetic acid are converted to the higher fatty acids."

Recently, evidence of the chemical feasibility of these views has been forthcoming in the work of Kuhn and others on the condensation of acetaldehyde and crotonaldehyde to conjugated polyene aldehydes of higher molecular weight ; this has been shown to be possible in the presence of specially chosen catalysts, notably organic salts of weak acids such as piperidine acetate, etc. From condensation products of crotonaldehyde Kuhn *et al.*[56a] have isolated hexadecaheptaenal, $CH_3.[CH{:}CH]_7.CHO$, from which cetyl alcohol was obtained by reduction, whilst its condensation with malonic acid gave octadecaoctaenoic acid, $CH_3.[CH{:}CH]_8.COOH$, converted by hydrogenation into stearic acid (the first synthesis of this acid direct from a two-carbon chain compound). Similarly, F. G. Fischer *et al.*[56b] obtained octatrienal and dodecapentaenal, $CH_3.[CH{:}CH]_5.CHO$, converting the latter into lauraldehyde by reduction, and also obtaining tetradecahexaenoic acid, $CH_3.[CH{:}CH]_6.COOH$, from it by further condensation with malonic acid. The way, chemically speaking, is therefore clear for the production of higher fatty acids of " even number " carbon content from acetaldehyde as starting point. Kuhn [56c] has pointed out the implications and reservations of these experiments in relation to the synthesis of fatty acids in the plant from acetaldehyde derived from hexose fermentation. It is evident that, if this be the fundamental mechanism, reduction of the polyene chain commences at a very early stage in the living plant since, by the time a C_{16} or C_{18} compound is reached, the colour of the conjugated polyene derivatives is intense and would necessitate far deeper coloration in the developing seed than is actually the case. There is, however, one very interesting feature to be noted if it be assumed, for the moment, that octadecaoctaenal, $CH_3.[CH{:}CH]_8.CHO$, is an intermediary precursor of C_{18} acids in fats synthesised *in vivo* : stepwise reduction of the conjugated system in this compound, in accordance with the Thiele rule, would add successive atoms of hydrogen at the extreme ends of the chain of conjugated ethenoid groups, and in this way would reach, at the stage immediately preceding complete saturation (stearic acid), the compound Δ^9-octadecenoic (oleic) acid. This is the only proposition put forward so far which leaves open the possibility of a selective synthesis of oleic acid.

It is interesting also to note here, whilst referring to Kuhn's recent work, that Takei *et al.*[57] have identified Δ^2-hexenal, $CH_3.[CH_2]_2.CH{:}CH.CHO$, and *trans*-$\Delta^4$-hexenol, $CH_3.CH{:}CH.[CH_2]_2.CH_2.OH$, in the growing leaves of tea, ivy, clover, oak, wheat, and other plants, whilst they state that certain diethenoid alcohols and aldehydes of the C_9 series are present in cypress and violet leaves, and in cucumbers.

Interesting additional insight into some aspects of fatty acid synthesis in animals is being acquired by studying the distribution of deuterium in the depot fatty acids of rats or mice which have been given " heavy water," D_2O, with their diets. This method of investigation, initiated by Schoenheimer and Rittenberg,[58] is at the time of writing being pursued by a number of workers. It is only possible here to mention some of the more interesting findings so far reported.

Schoenheimer and Rittenberg [58] found in 1936 that, when the body fluids of mice contain a proportion of " heavy water " the depot glycerides also contain deuterium in their acyl chains ; the deuterium contents of the stearic and palmitic acids present are about the same, and are greater than that of the unsaturated acids. It was also found that the rate of deposition and removal of depot glycerides is comparatively rapid. The deuterium content of the fats rose to a maximum in about six days (on a fat-free diet), and the " half-lifetime " of a fatty acid radical in the depots was only 5–9 days. Bernhard and Schoenheimer [59a] in 1940 confirmed these results with mice on a fat-free diet of bread and " heavy water," again finding that the saturated acids contained more deuterium than the unsaturated acids, but also noting that deuterium was absent from any di- or tri-ethenoid acids found to be present in the body fats. This suggests (*cf.* pp. 80, 98) that, unlike the saturated and mono-ethenoid acids, the polyethenoid acids are not synthesised by the animal, but are derived directly from dietary fats. These authors [59b] also showed that fat-formation from non-lipid sources is most rapid in the liver, followed by the " intestinal wall and kidney." Bernhard and Bullet,[60] in a similar study of rats fed on a diet rich in carbohydrates, confirmed that the " half-life period " of fatty acids in the depots is about nine days, and that one out of every two hydrogen atoms in the synthesised saturated fatty acids is derived from the water in the body.

On the other hand, they found that the synthesised oleic acid contained only about 40 per cent. of the deuterium content of the saturated acids, suggesting that oleic acid is synthesised in a different manner from the saturated acids. Boxer and Stetten[55] observed a similar difference between the deuterium content of the saturated and oleic acid in rats fed on a high carbohydrate diet with "heavy water," and inferred therefrom that saturated acids are the primary products of fatty acid synthesis.

Rittenberg and Bloch[61] fed rats and mice on special diets containing sodium acetate in which the hydrogen was replaced by deuterium, whilst the carboxyl carbon atom was the carbon isotope of atomic weight 13. They found that this sodium acetate was utilised in the body synthesis of fatty acids, and that in the fatty acid carboxyl groups the concentration of carbon of atomic weight 13 was approximately twice that in the whole molecule, suggesting that fatty acids are synthesised in the animal by successive condensation of C_2 units.

Sperry and Waelsch[62] supplied "heavy water" to rats for some days and then examined the unsaponifiable matter of the lipids in the body fat, when they found evidence of hydroxy- and keto-compounds containing deuterium which, they suggest, may be intermediate stages in the synthesis of fatty acids. No precise indication of the nature of these compounds was, however, put forward and it is therefore uncertain whether they form the first observation on record of the detection of a synthetic product intermediate between carbohydrate (or rather, perhaps, pyruvic acid or acetaldehyde) and fatty acids..

In the earlier forms of the aldol-condensation theory outlined above, it was generally taken for granted that saturated acids were the normal end-product, and that any unsaturated acids—including, of course, the chief components of all natural fats, oleic and linoleic acids—must be produced by "desaturation" of saturated acids. On this hypothesis, therefore, stearic acid is the inevitable precursor of oleic, linoleic, or linolenic acids—a proposition which bristles with difficulties. Not only have we to explain the widespread occurrence, in vast quantities, of a particular oleic acid, *cis*-Δ^9-octadecenoic acid (and of the similar linoleic or *cis*-*cis*-$\Delta^{9,12}$-octadecadienoic acid), but to account, in many cases, for the production of these acids in cool climates, where it is evident that the presence, even transiently, of stearic acid as an intermediate in any quantity would lead to the presence of fatty compounds which would be solid at the prevailing temperature.

These and other difficulties were appreciated at the time the original hypotheses were put forward. We may quote, for example, Leathes and Raper,[63] who express the opinion that it seems improbable that the saturated acids are the intermediate and the unsaturated acids the final products of biosynthesis, because the saturated acids first formed would be relatively more stable than the unsaturated acids; the saturated acids contain a greater store of potential energy than the unsaturated ones, and it does not seem clear why a substance stored up as a source of energy should be made first with a maximum store and then partially degraded to one with a lower potential energy by an oxidation process. These authors add that it is almost certainly proved (*cf.* this chapter, p. 376) that a process of "desaturation" takes place when reserve fat is called upon to yield up its energy, but that it appears unlikely as a process which operates in the synthesis of unsaturated acids previous to their storage as neutral fat. Leathes and

Raper also consider the possibility that fats are formed in nature by a series of reactions, the end points of which vary according to the temperature at which they occur; they suggest that at higher temperatures the reactions leading to the formation of higher saturated fatty acids may reach completion, while at lower temperatures the same end point is not reached, the unsaturated fatty acids then forming the final products. It will be seen that, on this view, the unsaturated acids are regarded as the intermediate, and the saturated acids as the ultimate, products of synthesis.

Apart from the difficulty of accounting for the production of Δ^9-octadecenoic (oleic) and its related unsaturated acids, all of the above theories of fatty acid synthesis based on assemblage of carbon atoms, in 2 or multiples of 2 at a time, share the disadvantage of failing to show (i) why the condensation should stop preferentially, as it does in so many instances (notably in animals) at the C_{16} or C_{18} stage, and (ii) why large quantities of acids such as lauric (C_{12}), myristic (C_{14}) or arachidic (C_{20}) should in other specific cases be preferentially produced. Accepting, for example, the proviso that fats in a living organism must be liquid, or almost liquid, at the prevailing temperature, it is clear that large quantities of glycerides of saturated acids will only be encountered in seed fats of tropical or sub-tropical plants; but it still remains to account for the preferential production of, for instance, lauric acid in the coconut and other palm fruits, and stearic acid in fats such as cacao butter, shea butter, and the like.

We must next briefly consider an approach to the problem from another angle, namely, that fatty acids may be produced by the direct condensation and subsequent transformation of monosaccharide molecules. This possibility has been realised for quite as long a time as the alternative of prior degradation of hexose to C_2 units which has already been discussed, and was supported by Emil Fischer.[64] This obviously accounts readily, on paper, for the production of C_{18} and C_{12} acids but, like the other view, takes no account of the specific formation of oleic and its related acids, and does not help much, in its simplest form, to explain the formation of palmitic and other saturated acids. At the same time, it is evident that palmitic acid could be envisaged as the end-product formed from two molecules of pentose and one of hexose. This is of course speculative, because no clear evidence has been given at present as to whether pentoses can be converted into higher fatty acids by enzyme action. They are present, of course, equally with hexoses in nature—in plants in the form of pentosans and gums derived from *d*-xylose and *l*-arabinose, and in animals in the nucleoproteins (*d*-ribose), and in both in the form of nucleic acids (*d*-ribose).

Armstrong and Allan [65] supported the direct monosaccharide condensation hypothesis in a theoretical survey of the problem some years ago, and also suggested a further alternative: the resolution of a hexose into C_3 (instead of C_2) units, followed by condensation of C_3 units to C_6, C_9, C_{12}, C_{18}, etc., units of a fatty nature, pointing out that in such a process oleic acid might be one of the ultimate products. The conception of C_3 units, at first sight unusual, is at all events in harmony with the current views of carbohydrate fermentation (alcoholic), in which it is now recognised that triosephosphoric acids play an important part as intermediate products. It is certainly attractive because of the leaning towards C_3, C_6, and C_9 groups which is so clearly observable in the natural unsaturated fatty acids. Examples of this are as follows:

TYPE	GROUPING	ACIDS IN WHICH THIS GROUPING OCCURS
C_9	$CH_3.[CH_2]_7.CH=$ or $=CH.[CH_2]_7.COOH$	Oleic, linoleic, linolenic, elæostearic, hexadecenoic, tetradecenoic, ricinoleic, erucic, (also oleyl alcohol).
C_3	$=CH.CH_2.CH=$	Linoleic, linolenic.
C_6	$CH_3.[CH_2]_4.CH=$ or $=CH.[CH_2]_4.COOH$	Linoleic, petroselinic.
C_{12}	$CH_3.[CH_2]_{10}.CH=$	Petroselinic.

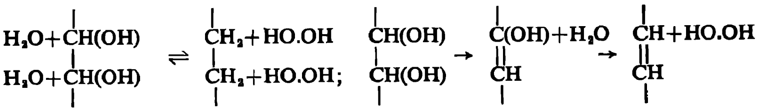
More or less direct formation of fatty acids from hexoses is perhaps also supported by the observations of Emde[66] and Reichel[50] that a specific hexose, fructose, is more readily converted than others into fatty acids. On the other hand, it is apparently not in harmony with the findings of Haehn and Kinttof[47] that carbon dioxide is consistently formed during the conversion of sugars into fats—this latter observation pointing definitely towards the initial breakdown of hexose into acetaldehyde and carbon dioxide.

Those who favour the theory of initial production of C_{18} acids from three molecules of hexose have frequently attributed the occurrence of acids of lower molecular weight to degradation of the C_{18} acid by what is known as β-oxidation :

$$R.CH_2.CH_2.COOH \rightarrow R.CO.CH_2.COOH \rightarrow R.COOH+2CO_2+2H_2O$$

(a process which would, incidentally, involve the formation of carbon dioxide). "β-Oxidation" of fatty acids is a process which has been conclusively proved to occur during their disruption in the animal organism, but this is not necessarily evidence that it takes place during their synthesis. Moreover, it does not help us to explain the biosynthesis of palmitic or lauric acids from the unsaturated oleic acid which, as the most prevalent natural C_{18} acid, may reasonably be supposed to be the fatty acid produced in the first instance from sugars. Actually, Armstrong and Allan (*loc. cit.*) said that, when hexa- or tetra-decenoic acids accompany palmitic acid in a fat (e.g. marine animal oils), they were inclined to accept β-oxidation as the probable mechanism of production of the abundant palmitic acid ; but that in other cases some other explanation to account for its direct synthesis seems desirable. In the light of later knowledge, even this qualified acceptance of β-oxidation must go by the board, for both hexa- and tetra-decenoic acids are known to contain their unsaturation in the same position (Δ^9-) as oleic acid, whereas their production from the latter by β-oxidation would lead respectively to a Δ^7-hexadecenoic and a Δ^5-tetradecenoic acid !

On the other hand, the mechanism of the initial stages of the β-oxidation process, applied to other parts of the alkyl chain, may well play an important part (in the reversed direction) in the transformation of a $-CH(OH).CH(OH)-$ carbohydrate grouping into $-CH_2.CH_2-$ or $-CH{:}CH-$, for instance :



$$\begin{array}{cccccccc} | & & | & | & & | & & | \\ H_2O+CH(OH) & & CH_2+HO.OH & CH(OH) & & C(OH)+H_2O & & CH+HO.OH \\ | & \rightleftharpoons & | & | & \rightarrow & \| & \rightarrow & \| \\ H_2O+CH(OH) & & CH_2+HO.OH; & CH(OH) & & CH & & CH \\ | & & | & | & & | & & | \end{array}$$

Thus, a typical carbohydrate system might undergo conversion (reduction) into a typical fatty system by the operation of an oxidation-reduction process in which hydrogen peroxide (or atomic oxygen) would be released and utilised by an "oxygen acceptor" present in the reacting system.

It will be seen that the results of speculative contemplation as to the possible mode of conversion of sugars into fats lead to a number of suggestions, none of which is at present either adequately supported by experimental evidence, or free from a number of difficulties. Perhaps it will be helpful to set down the chief suggestions in a tabular form which, whilst obviously only illustrative, may serve to recapitulate what has been discussed in the previous pages :

GENERAL HYPOTHESIS	TYPES OF POSSIBLE FATTY ACIDS
(*a*) Aldol-condensation+reduction (i) of acetaldehyde (Nencki, Smedley-MacLean, Haehn, etc.).	Saturated acids of the series $C_{2n}H_{4n}O_2$.
(*b*) Aldol-condensation+reduction (ii) of crotonaldehyde and acetaldehyde (polyene aldehydes) (Kuhn, Reichel, etc.).	Saturated and unsaturated acids of the series $C_{2n}H_{4n}O_2$: $3C_4 \rightarrow C_{12}$; $3C_4+C_2 \rightarrow C_{14}$; $4C_4 \rightarrow C_{16}$; $4C_4+C_2 \rightarrow C_{18}$; etc.
(*c*) Direct condensation of hexoses (E. Fischer).	$3C_6 \rightarrow C_{18}$.
(*d*) Condensation of 3-carbon units produced from hexoses.	Possible unsaturated acids with the characteristic groupings $=CH.CH_2.CH=$, $=CH.[CH_2]_7.C-$, etc.
(*e*) Direct condensation of hexoses and/or pentoses.	$2C_6 \rightarrow C_{12}$; $2C_5+C_6 \rightarrow C_{16}$; $3C_6 \rightarrow C_{18}$; $4C_5 \rightarrow C_{20}$; $2C_5+2C_6 \rightarrow C_{22}$; etc.

Oleic acid can be accounted for by mechanisms (*b*), and possibly (*c*) and (*d*) ; saturated acids not multiples of C_6 (i.e. the myristic, palmitic, arachidic, etc., series) can be accounted for, without recourse to oxidative degradation of a higher acid, by mechanisms (*b*) or (*e*) ; mechanism (*e*), which must in any case be regarded as purely speculative in the absence of experimental evidence as to pentose fermentation to fatty acids, fails curiously to allow for the production of acids of the C_{14} (myristic) series.

There are many details, however, which are still difficult to reconcile with any simple mechanism of conversion of carbohydrate to fatty acid ; of these the following may be mentioned :

(i) When one saturated acid occurs in comparatively large amounts as a major component of a fat, it will almost always be found that minor quantities of the acids containing two more and two less carbon atoms in the molecule accompany it. Thus, the many liquid fats which contain about 7–10 per cent. of palmitic acid as a characteristic component also usually contain small amounts (not more than 1–2 per cent.) of myristic and stearic acid ; in palm oils with about 40 per cent. of palmitic acid there is usually about 2 per cent. of myristic and 4–6 per cent. of stearic acid ; in seed fats containing large proportions of stearic acid there is usually a little arachidic as well as palmitic acid ; the Palmæ kernel fats with 45–50 per cent. of lauric acid contain also about 20 per cent. of myristic and about 6–8 per cent. each of caproic and caprylic acids ; the palmitic acid (usually 10–15 per cent.) of fish oils is accompanied by about 2–5 per cent. of myristic and up to 1 per cent. of stearic acid.

The production of the next lower acid in the natural series than the major component acid could be " explained " by recourse to the β-oxidation mechanism ; but almost always the acids on *both* sides of the major component saturated acid (i.e. of higher as well as of lower molecular weight) are in evidence. The phenomenon is, indeed, rather that of an exceedingly sharp maximum formation of one (the " major component ") acid, with very small amounts of the adjacent members of the saturated homologous series.

(ii) In a few groups of seed fats, especially those of the Palmæ, there is a relatively long sequence of saturated acids, rising in content to a sharp maximum and then falling. For example, in the saturated fatty acids of the coconut, we have :

ACID:	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
PER CENT.	Trace	9	8	52	19	10	2

In most cases of this kind the proportion of oleic acid present is unusually low, and one is tempted here to fall back upon the older Nencki and Smedley view that, at least in these saturated acids, the synthesis is the result of a step by step building-up from C_2 units with a selective preference for a maximum production of one acid. This would also include the otherwise unaccounted for group of *Myristica* fats (of high myristic and low oleic content) and would in addition serve to explain the general presence of small amounts of the two adjacent acids to a major saturated component acid to which attention has just been drawn. Yet on general grounds, as has been pointed out in the course of this discussion, it seems at the moment equally reasonable to look to C_6 and C_3 (with perhaps C_5) carbohydrate-like complexes for a more consistent explanation of fat synthesis in the majority of cases.

(iii) The marked tendency for animals to synthesise reserve fats containing a very large proportion of palmitodi-C_{18} glycerides (probably originally mainly palmitodiolein) is a characteristic feature which clearly invites a special explanation in terms of the derivation of palmitodiolein—or, at least, a mixture of one molecule of palmitic acid and two molecules of oleic acid—from carbohydrate.

(iv) The milk fats, with their characteristic content of butyric-lauric acids, represent another group which demands separate consideration. From what has been said earlier, however, it will be appreciated that there is growing reason to consider that, in their final form, both the reserve and milk fats represent mixtures of glycerides which have undergone specific modifications in the organism subsequent to the synthesis of the original fatty acids and their combination into the precursor glycerides of the final fats.

It will be seen that the problem of the synthesis of fats *in vivo* from carbohydrates is extraordinarily complex and difficult. There are so many varieties of fat components that it is not at all easy to make a logical and clear statement of the case, quite apart from the lack of ascertained facts and the uncertain premises of many of the suggested hypotheses. The foregoing arguments may be summed up by saying that there is general and apparently well-founded belief that carbohydrates, and indeed hexoses, are the chief precursors of fats synthesised in plants and animals ; and that a number of suggestions have been made as to the chemical processes through which the conversion into fat may be effected. Relatively few of these hypotheses have accorded sufficient weight to consideration of the different characteristic groups of component acids which are known to be representative of various natural biological groups of fats ; yet some consistent explanations have been put forward which allow for the widespread occurrence of oleic acid, the production in specific instances of other C_{18} (and C_{12} or C_{24}) acids, and for the possibly independent production of C_{14}, C_{16}, C_{20}, or C_{22} acids.

If one or other of the sequences of processes suggested above should prove to be a rudimentary approximation (and, with our present knowledge, it can be no more) to the biochemical conversion of carbohydrate into fatty derivatives of the nature of oleic and linoleic acids, there nevertheless still remain a number of difficult problems to solve before the origin of the curiously specific mixtures of components which characterise the fats of different groups in the biological world receives a rational and adequate explanation.

The Assimilation of Preformed Fats by Animals

When preformed fats form part of the diet of an animal, they are dealt with, not in the liver, but in the epithelial cells (villi) of the small intestine. From these, the fats which are absorbed by the animal pass into the lymph or chyle which flows through the lacteals of the small intestine into the thoracic duct and finally emerges into the blood stream. This peculiarity has rendered the fate of ingested fat more amenable to experimental study than the allied problem of fat synthesis in the animal; and possibly has led to somewhat disproportionate stress being laid at times upon the formation of fat in animals by direct assimilation. The results of investigations by many workers (especially those of Munk from about 1880 to 1900) went to show that ingested fat is not directly absorbed into the lymphatic system, but is first hydrolysed and then resynthesised into glycerides; Moore [67] proved definitely that this process takes place in the epithelium of the small intestine before the lacteal glands are reached. That the ingested fat is first broken down was indicated, not only by the fact that other materials such as hydrocarbons [68a, 68b] which might be expected to pass into the chyle are merely excreted, but also by the facts that administration of waxes such as cetyl palmitate,[69a] or of ethyl esters of fatty acids,[69b] leads to the appearance only of glycerides in the chyle. Hard fats (e.g. mutton fat) may lose some of their more saturated components, and liquid fats may become somewhat more saturated,[68b, 69a, 69c] during the process. At one time it was considered that the fatty acids were entirely absorbed as soaps, but later it was more generally held that the absorption proceeds mainly *via* the fatty acids,[70a] perhaps partially present as soaps, but that it is certainly promoted by the solvent action of the bile acids [70b] and, perhaps, of other substances such as lecithin which may be present.

The preceding statement sums up very briefly the views generally accepted with regard to fat assimilation by animals up to about the present time; in a word, the ingested fat is hydrolysed by lipase in the villi of the small intestine, passes as free fatty acids (or soaps) into the chyle, and is resynthesised into glycerides which pass on to the thoracic duct. In its more recent development (Verzár *et al.*,[71] 1936), the view that lipolysis is an essential preliminary to fat absorption supposes that the fat is first completely hydrolysed, and then resynthesised in the intestinal cells with the aid of intermediate phosphorylation (i.e. by the intermediary of phosphatides).

Recent work by Frazer,[72] however, suggests that this explanation requires considerable modification. Frazer [73] utilised a method of tracing the glycerides present in body-fluids (blood) by microscopic observation ("chylomicrography"), employing dark-ground illumination which permitted the particles of unhydrolysed fat (glycerides) to be detected and counted. In this way the sequence of events consequent upon ingestion of fatty meals, or of olive or other fatty oil, was followed. It was found that hydrolysis takes place, but only partially; and that the *unhydrolysed fat* passes directly as such by the lacteal-lymphatic system and thence to the fat depots, whilst the fatty acids formed pass by the capillaries and the portal vein to the liver where they may be further metabolised. In support of this it was found that a diet of neutral fat with added lipase caused an effect similar to that associated with the ingestion of fatty acids ; whereas complete inhibition of lipolysis by added sodium cetyl sulphate did not interfere with the triglyceride absorption into the lacteals, thus suggesting again that lipolysis is *not* an essential step in fat absorption. Frazer's explanation is therefore that ingested fat which is to be deposited as reserve fat by the animal is directly absorbed (without intermediate hydrolysis and resynthesis) *via* the lymphatic system ; lipolysis (i.e. resolution into free fatty acids) is not connected with fat deposition, but with the production of fatty acids which pass into the liver ; lipolysis thus regulates the fate of absorbed glycerides and thus may also provide fatty acids for soap and phosphatide formation.

It may be noted that it is difficult, on the older view, to understand how the unsaponifiable matter (including the fat-soluble vitamins) in ingested fats reaches the liver, but that this is readily explicable in the light of Frazer's theory, since unsaponifiable substances, like the fatty acids produced by lipase hydrolysis, are soluble or dispersible in bile acid solutions and thus pass with the fatty acids to the liver.

Frazer and Sammons[74] (1945) have studied the hydrolysis of olive oil with pancreatic lipase over four-hour periods, and have demonstrated that the free fatty acid liberated is not accompanied by the equivalent amount of free glycerol ; on the contrary, the acetyl value of the unhydrolysed portion rises to a figure equivalent to a content of at least 20–25 per cent. of monoglyceride, indicating that the hydrolysis proceeds in stages and is far from complete in the period of normal digestion of fat. They also showed that bile salt—fatty acid—monoglyceride provides a complex which is an emulsifying system for neutral triglycerides, and which is stable over the pH range of 5·0–9·0. Brown and Shrewsbury[75] had shown earlier (1941) that monostearin or monolinolein can be utilised by rats in the elaboration of triglycerides, and that the ingested monoglycerides appear in the depot fat as triglycerides.

G. O. Burr *et al.*,[76] using maize oil acids which had been isomerised by alkali to conjugated octadecadienoic acids, traced the passage of these into phosphatides and neutral fat in the intestinal mucosa by spectrographic observation, and thereby showed that there was no correlation between the rate of transport of fat and the incorporation of the fatty acids into the mucosal phosphatides. This may be regarded as evidence against the direct chemical intervention of phosphatides in the process of fat absorption.

From the detailed component acid analyses of depot fats of animals which received fatty diets it is easy to appreciate, firstly, that fatty acids not synthesised by the animals are readily absorbed without alteration from ingested fats and, secondly, that quite frequently the normal course of fat synthesis has been clearly disturbed as a result of the fat ingested. Evidence on these lines as to the general effect on the depot glycerides—additive or otherwise—is by no means so clear. Study of the glyceride structure in such cases has not yet been systematically made, and it seems probable that knowledge of the component glycerides, rather than the fatty acids, would throw more light on the final effect of, at all events, heavy administration of ingested fats to animals.

The effect on depot fat component acids of fats taken in the diets of animals was dealt with in Chapters II and III, where data were available, following the more normal types of reserve fat in each animal. The chief instances are recapitulated in Table 97 (p. 371).

Instances in which acids present in the ingested fats (but not normally in the depot fats of the animals concerned) appeared in the latter include the beetle studied by Collin, Miss Cruickshank's hens and their eggs (the latter only in the case of linolenic acid from linseed or hempseed), the crab *Birgus latro*, rats (in the cases of cod liver, cottonseed, coconut, palm, and olive oils), pigs (soya beans, groundnuts, menhaden oil), dog (rape oil), whilst some of the specific acids of rape and cod liver oils appeared in the milk fats of cows receiving these fatty oils.

The examples of interference with the normal composition of animal depot fats as a result of ingestion of dietary fat are perhaps more interesting. Amongst these may be recalled the effects of feeding cottonseed oil to the extent of 8 per cent. or more of the diet of pigs (Ellis, Rothwell, and Pool),[86] and of feeding rats on diets containing 40 per cent. of beef fat or palm oil; in these cases the palmitic acid content of the depot fat fell below both (i) the normal figure for that of the animal on a low-fat diet, and (ii) the palmitic acid content of the ingested fats themselves. This, of course, indicates on the one hand inability to absorb all the palmitic acid contained in the dietary fats and also interference with the normal composition of the (mainly synthetic) depot fat of the animal.

Similarly, the ingestion of some fatty oils (especially cod liver oil) by cows causes marked alterations in the component acids of their milk fats, although in this case the amount of any acid specific to the ingested fat which appears in the milk fat is relatively small.

The opposite effect is noticeable in the two instances cited of fish fats, where Lovern [77a, 77b] has shown that modification (usually hydrogenation) of the ingested fat may take place during or after its deposition in the flesh of the eel or herring. Lovern [77c] also fed ethyl palmitate or ethyl myristate to eels: the former caused considerable increase in the palmitic and hexadecenoic acid contents of the depot fat, the latter gave rise to smaller increases in tetradecenoic and palmitic acids (this apparently by compensating hydrogenation of hexadecenoic acid already present in the eel depot fat).

It has been mentioned in earlier parts of this book that saturated acids with less than 10 or 12 carbon atoms are not stored in animal reserve fats. Longenecker [85] showed, by feeding coconut oil to rats, that their depot fatty acids included 27 per cent. lauric and 0·5 per cent. decanoic, compared with 45 per cent. lauric, 8 per cent. decanoic, 5 per cent. octanoic, and 0·8 per cent. hexanoic in the fatty acids of the ingested coconut oil. This confirms the findings of Longenecker and Hilditch,[84] Channon, Jenkins, and Smith,[82] and previous workers who administered butter fat to various animals. Using tributyrin which was "labelled" with deuterium, Morehouse [92] showed that ingested tributyrin appeared transiently in the tissue fats, but disappeared therefrom completely after 36 hours; further, it was not converted into long-chain fatty acids.

Other investigators [93] have studied the assimilation of fats or fatty acids containing straight chains with an odd number of carbon atoms in the molecule, in the cases of dogs, young goats, and rabbits. The odd-numbered acids, from $C_{13}H_{26}O_2$ onwards, were assimilated and appeared in the fat depots, apparently as readily as the even-numbered acids of similar molecular weight.

TABLE 97

FAT	ANIMAL GROUP	SPECIES	INGESTED FATS	INVESTIGATOR	CHAP.	PAGE
Flesh	Fish	Herring	Chiefly copepods	Lovern [77a]	II	39
,,	,,	Eels	Herring, mussel	Lovern [77b]	II	48
Body	Invertebrate	Hermit crab (*Birgus latro*)	Coconuts	Hilditch and Murti [78a]	II	29
,,	Insects	*Pachymerus dactris*	*Manicaria saccifera*	Collin [78b]	III	68
Depot	Birds	Domestic hen; also egg (yolk).	Palm kernel oil, hempseed oil, or mutton tallow.	Cruickshank [79]	III	73, 77
,,	,,	Sea-birds	(?) Fish fats	Lovern [80]	III	74
,,	Rodents	Rat	Cod liver oil	Banks *et al.*,[81] Channon *et al.*[82]	III	81–84
,,	,,	,,	Cottonseed oil	Spadola and Ellis [83]	III	,,
,,	,,	,,	Butter, beef depot, and various vegetable fats.	Channon *et al.*[82]	III	,,
,,	,,	,,	Cow milk fat	Longenecker and Hilditch [84]	III	79
,,	,,	,,	Coconut oil, maize oil	Longenecker.[85]	III	82
,,	Herbivora	Pig	Soya bean, groundnut	Ellis and Zeller [86a]	III	100
,,	,,	,,	Cottonseed oil	Ellis *et al.*[86b]	III	100
,,	,,	,,	Menhaden oil	Brown [87]	III	101
,,	,,	,,	Low-fat diet	Hilditch *et al.*[37]	III	95
,,	,,	Ox	Soya bean, maize, coconut, menhaden oils.	Thomas *et al.*[88]	III	101
,,	Carnivora	Dog	Linseed oil, mutton tallow	Lebedev [89]	III	101
,,	,,	,,	Rape oil	Munk [90]	III	101
Milk	Herbivora	Cow	Coconut, soya bean	Hilditch and Sleightholme [91a]	III	119–123
,,	,,	,,	Linseed, rape, cod liver oils	Hilditch and Thompson [91b]	III	,,

Glycerides of specific acids have frequently been deliberately employed as a means of "labelling" or tracing ingested fats in the depots and other tissues of the animal body. Of the natural fats, cod liver oil with its highly unsaturated C_{20} and C_{22} acids, and rape oil with a high content of erucic acid, have often been used in this way, whilst glycerides of the artificially prepared elaidic acid or containing "*iso*oleic" acids of hydrogenation have been utilised. Sinclair,[32b] especially, has made systematic use of ingested elaidic glycerides in studying fat metabolism.

The use of deuterium has been explored considerably to the same end by Schoenheimer and Rittenberg,[94a] who have obtained some remarkable results. Their evidence goes to show that ingested fats are not utilised directly for energy (oxidation), but are first deposited in the depots and subsequently mobilised therefrom. When mice were fed with ethyl (deutero)stearate (produced from linseed oil by hydrogenation with deuterium), their body fats contained (deutero)unsaturated acids, indicating desaturation of stearic to unsaturated acids or glycerides. Also, when the (deutero)unsaturated acids extracted from these animals were fed as esters to another group of mice, (deutero)stearic acid appeared in the body fats of the latter, indicating that hydrogenation of ingested fats may take place. In another experiment it was shown that ingestion of ethyl (deutero)stearate by mice leads to the presence in the depot fats not only of (deutero)stearic and (deutero)-unsaturated acids, as mentioned, but also of (deutero)palmitic acid ; this is considered to show that stearic acid is converted in the animal into palmitic acid. On the other hand, ingestion of esters of (deutero)butyric and *n*-(deutero)hexanoic acid caused no introduction of deuterium into the depot fats. This confirms the previously known fact that the saturated acids of lower molecular weight than myristic are not laid down as depot glycerides, and in addition the authors conclude that the results prove that the higher acids are not formed in the animal by building up from butyric or *n*-hexanoic acid ; in their own words, butyric and *n*-hexanoic acids are not fat-formers (*cf.* above, Morehouse [92]).

The use of this method is, of course, only recent, and it is not yet possible to be too certain of the interpretation of the results ; the difficulties and the caution necessary in interpretation have been emphasised by Schoenheimer [94b] and by Bonhoeffer.[94c] There is still open the possibility that deuterium in an acyl group may be exchanged for ordinary hydrogen in the body, so that negative findings of deuterium are indecisive. Positive results, on the other hand, have so far been accepted as decisive ; but, since Schoenheimer *et al.*[94d] have shown that palmitic acid can acquire deuterium by contact with deutero-sulphuric acid, there seems to be uncertainty at present as to whether such exchanges might take place as the result of enzyme actions in the body. This might of course affect the explanation of the experimental findings.

Digestibility of ingested fats. Glycerides containing a wide variety of fatty acids (from butyric to arachidic, or from hexadecenoic and oleic to the highly unsaturated C_{22} acids) seem to be equally readily dealt with by animals. So long as the ingested fat is liquid at the temperature of the digestive tract, the specific nature of the natural fatty acids present is largely immaterial, so far as power of assimilation and utilisation is concerned. Fats of higher melting point are, however, dealt with with difficulty and are frequently excreted unchanged.

ASSIMILATION OF FATS BY ANIMALS

Animals normally excrete a certain proportion of fat, fatty acids (or their salts), and in certain diseased conditions the amount may be much increased When a normal healthy animal is fed with fats of high melting point, these are however excreted for the most part unchanged. Thus Arnschink [69c] found that the fæcal fat of dogs fed on mutton tallow was of higher melting point than the normal, that only about 10 per cent. of tristearin was absorbed when this was ingested alone, but that 90 per cent. or more of mixtures of tristearin with olive oil could be assimilated. Similarly Levites [95] states that, when administered separately as free fatty acids, 98 per cent. of oleic, 78 per cent. of palmitic, and only 35 per cent. of stearic acid was absorbed, although when given as the separate sodium salts, the amounts absorbed were sodium oleate 100, sodium palmitate 90, and sodium stearate 87 per cent. Recently, Mattil and Higgins,[95b] whilst confirming the poor assimilation of tristearin (even when fed along with tri-olein) have observed that mixed stearo-oleo-glycerides are also relatively poorly digested, although better than tristearin itself.

Wesson,[96a] Holmes,[96b] and Langworthy [96c] have determined the " digestive coefficients " of a large number of fats for human beings. Vegetable oils and soft fats (e.g. coconut or palm oils, cacao butter), the softer animal fats (such as butter, chicken fat, lard, beef suet), and cod liver oils all have coefficients of 95 per cent. or over, usually 97–99 per cent. Definitely lower coefficients were observed with mutton tallow (88·0 per cent.), deer fats m.p. 52–53° (81·7 per cent.), and " oleostearin," m.p. 50–56° (80·1 per cent.). The figures quoted by Langworthy for some hydrogenated fats are exceptionally interesting in illustrating the effect of melting point on digestibility :

HYDROGENATED MAIZE OIL		HYDROGENATED COTTONSEED OIL		HYDROGENATED GROUNDNUT OIL	
M.P.	COEFFICIENT OF DIGESTIBILITY	M.P.	COEFFICIENT OF DIGESTIBILITY	M.P.	COEFFICIENT OF DIGESTIBILITY
(Original oil)	96·9	(Original oil)	97·6	(Original oil)	98·3
33·0°	94·7	35·0°	96·8	37·0°	98·1
42·0°	95·4	38·6°	95·5	39·0°	95·9
50·0°	88·5	48·0°	94·9	43·0°	96·5
				50·0°	92·0
				52·4°	79·0

It is quite clear that digestibility declines only when the fat approaches a melting point of about 48–50°.

In this connection it should be recorded that a great many studies by a number of workers [97] have been devoted to animal-feeding trials (generally with rats) to determine whether natural cow milk fats are superior or not to the different kinds of fat-blends present in modern margarine or butter substitutes. Although in some few instances it appeared that growth was maintained somewhat better when butterfat was given, the great majority of the results go to show unequivocally that there is no significant difference in nutritive value between butter, margarine, or the vegetable oils (such as groundnut, cottonseed, etc., oils) one or more of which is usually present in quantity in margarines. It is interesting also to recall that human milk fat, in its component acids and glycerides, has been shown [98] to resemble the softer varieties of margarine much more closely than it does cow milk fat ; in particular, it contains little or no acids with less than 12 carbon atoms in the molecule.

Ingested fatty acids essential to health. Finally, reference may again be made to certain unsaturated fatty acids, especially linoleic acid, which appear to be essential to health but which are apparently not synthesised by, at all events, certain animals. The most clear-cut instance is the rat, which develops specific diseased conditions if it is unable to obtain linoleic glycerides in its diet (Burr and Burr).[29] It is also almost certain that linoleic glycerides are not synthesised by the pig, which probably only deposits these in its depot fats as the result of ingestion from cereal, etc., meals [27, 86a]; although no definite evidence yet exists to show that absence of linoleic glycerides affects the health of the pig.

That it is the presence of a certain amount of polyethenoid glycerides which is necessary to the health of the rat follows from the work of Turpeinen,[99] who found that, whilst small doses of methyl arachidonate or linoleyl alcohol cured the symptoms of fat-deficiency, methyl or ethyl esters of Δ^{12}-octadecenoic, ricinoleic, erucic, and chaulmoogric acids failed to do so. That only certain polyethenoid derivatives can play the essential role of linoleic acid is seen in the work of Karrer and Koenig,[100] who found that $\Delta^{9,11}$-octadecadienoic, $\Delta^{10,13}$-nonadecadienoic, $\Delta^{11,14}$-eicosadienoic, Δ^{2}-phytenoic, and $\Delta^{2,6}$-phytadienoic acids were all ineffective.

Biochemical Transformations of Fats

It is beyond the scope of a work dealing with the chemical structure of natural fats to consider in any detail the fate of these products as a result of their subsequent destruction, either by the normal processes of their utilisation in plants or animals (mobilisation), or as a result of the action of enzymes or of atmospheric oxygen upon fats after their isolation from tissues (rancidity). A very brief outline of the chief features of both of these general processes may, however, be of service.

THE MOBILISATION OF RESERVE FATS

(*a*) PLANTS (SEEDS)

Fat stored in the endosperm or embryo of a seed serves as part of the nutriment of the germinated plant, at all events until leaf (and chlorophyll) production permits the normal photosynthetic processes to operate in the seedling. Observations in this field indicate, on the whole, that changes which approximate to a reversal of the sequence of those which take place in the ripening seed occur during, or rather after, germination. As in the case of seed fat synthesis, much of the work on seed fat utilisation by the germinating seed is due to Ivanow.[101] It was known previously, however, that the seed fat does not disappear very rapidly in the first stages of germination ; during the initial development of the root and the succeeding growth of the cotyledons beneath, and until they reach, the surface of the soil, there is relatively little loss of fat from the seed.[102a] As soon as the cotyledons are fully expanded and chlorophyll has commenced to appear, fat disappears rapidly and at the same time the carbohydrate content of the seedling increases ; this is illustrated by Ivanow's data for linseed, poppy seed, and hemp seed on germination :

		IN ORIGINAL SEED PER CENT.	IN SEEDLINGS (AFTER GERMINATION) 4 DAYS OLD PER CENT.	8 DAYS OLD PER CENT.
Linseed	Fat	33·6	26·4	16·0
	Carbohydrate	4·5	6·7	17·6
Poppy seed	Fat	47·0	38·5	36·3
	Carbohydrate	1·2	6·8	17·4
Hemp seed	Fat	31·3	17·8	11·3
	Carbohydrate	2·8	7·9	10·2

Changes in unsaturation and free fatty acid content of the fat in the germinating seeds are, again, exactly the converse of those noticed during seed fat development (*cf.* pp. 342–346). In his studies on germinating linseed and poppy seed, Ivanow found that the fat content and iodine value of the fat changed as follows :

	LINSEED		POPPY SEED	
	FAT CONTENT PER CENT.	IODINE VALUE	FAT CONTENT PER CENT.	IODINE VALUE
In original seed	33·6	173·4	47·0	140·2
In seedling, 8 days old	16·0	93·4	36·3	71·6

The unsaturation thus falls with great rapidity so soon as the reserve fat in the seed commences to be used. At the same time, as du Sablon [102b] and others showed many years ago, the fat is steadily resolved into free fatty acids as soon as the cotyledons commence active growth ; this is, of course, attributable to the intervention of lipolytic enzymes which are always present in seeds.

Miller [103] made an extensive series of observations on the germinating seed of the sunflower, in the course of which he paid attention to the acetyl values of the ether-soluble extracts of the cotyledons and of the root ; compared with that of the seed fat, the former had decreased slightly, but the latter showed a considerable increase. Miller concluded that the introduction of hydroxyl groups into the acyl chain (hydroxylation at ethenoid bonds) was an integral phase in the conversion of fatty acids into their degradation products in the seed ; Ivanow,[101] on the other hand, ascribed the rapid fall in iodine value to the relatively more rapid disappearance of the more highly unsaturated acids.

There is clearly scope for much further investigation of the immediate transformation products of the seed fatty acids and, as Leathes and Raper [104] have remarked, the water-soluble (and other) acids which seem to represent intermediate stages between fatty acids and sugars would almost certainly well repay further and more detailed examination.

(*b*) THE MOBILISATION OF ANIMAL RESERVE FATS

Animals require fat as a source of energy or heat (i.e. by means of oxidation, ultimately, to carbon dioxide and water) and they also require a certain minimum of fatty compounds [*] in the various organs of the body (termed the " élément constant " by Terroine [105]), below which life cannot be maintained. Briefly, it may be said that the fat of an animal present in excess of this minimal amount (Terroine's "élément variable") is either utilised directly for oxidation and production of energy, or is excreted as such or after metabolic change, or is laid down as reserve fat in adipose tissues. There is, therefore, to a considerable extent, a condition of equilibrium as regards the fat present in an animal, the adipose tissues acting as reservoirs which are capable of storing up fat when the fat intake and fat synthesis in the animal produces quantities in excess of that required for energy production, and which, conversely, are able to supply fat for oxidation when the animal is not producing it or assimilating it in sufficient amount from the food.

Oxidation or other transportation processes of fats are unlikely to occur in the adipose tissue, and the first stage in the " mobilisation " of reserve fat is probably its release into the blood stream by the operation, in the reverse order, of the steps by which it was deposited therefrom in the adipose tissues (*cf.* this chapter, pp. 354, 368). The released reserve fats then pass to various parts of the body (especially muscular tissues) in which they undergo deep-seated changes and yield up their stored energy.

The oxidative degradation of fatty acid chains in the animal organism has been the object of much investigation. The classical work of von Knoop [106] and of Dakin [107] on the " β-oxidation " of compounds such as phenylacetic acid, β-phenylpropionic acid or δ-phenylvaleric acid in the intestinal tract of the dog clearly established that the following sequence of actions may take place:

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[*] Much of the fatty material composing the " élément constant " may well be phosphatide (phospholipid) and not glyceride.

$$R.CH_2.CH_2.COOH+O \rightarrow R.CH(OH).CH_2.COOH+O \rightarrow R.CO.CH_2.COOH \rightarrow R.CO.CH_3 \rightarrow R.COOH.$$

Leathes and Wedell[108] suggested, as an alternative initial mechanism, desaturation of the original acid as follows:

$$R.CH_2.CH_2.COOH \rightarrow R.CH{:}CH.COOH(+H_2O) \rightarrow R.CH(OH).CH_2.COOH.$$

It has thus been known for a considerable time that β-oxidation takes place under certain conditions in the animal and that the carboxyl carbon atom and that adjacent to it can be removed, leaving a new carboxyl group in place of the β-carbon atom in the original chain. It should be noted, however, that no experimental instance has been given of the conversion *in vivo* of a higher saturated acid into one containing two carbon atoms less, for example, of stearic into palmitic acid. In the utilisation of fatty acids in which β-oxidation is believed to play an important part, the acids disappear completely, and no acids of molecular weight intermediate between the original acid and the final products (carbon dioxide and water) have ever been definitely isolated. For this and other reasons, Jowett and Quastel[109] reinvestigated the oxidative degradation of fatty acids in living tissues, and were led by the results obtained to consider the process as one of "multiple alternate oxidation," i.e. oxidation at alternate carbon atoms throughout the length of the acyl chain:

$$CH_3.CH_2 \vdots CH_2.CH_2 \vdots CH_2.CH_2 \vdots CH_2.CH_2 \vdots CH_2.CH_2 \vdots CH_2.COOH.$$

On the other hand, Mackay *et al.*[110a] have suggested that during β-oxidation the two terminal carbon atoms involved are split off as acetic acid, which may undergo auto-condensation to yield acetoacetic acid and acetone:

$$CH_3.[CH_2]_n.CH_2.CH_2.COOH \rightarrow$$
$$CH_3.[CH_2]_n.COOH+CH_3.COOH, \text{ etc.}$$
$$2CH_3.COOH \rightarrow CH_3.CO.CH_2.COOH \rightarrow CH_3.CO.CH_3+CO_2.$$

This "β-oxidation-condensation" theory has been examined by Weinhouse *et al.*,[110b] who have studied the oxidation *in vivo* (sliced rat liver) of *n*-octanoic and *n*-butyric acids in which the carbon atom of the carboxyl group consisted of the "heavy" carbon isotope ^{13}C. They examined the ^{13}C content of the acetone, acetoacetic acid, and carbon dioxide produced by the oxidation. Both acetone and acetoacetic acid contained isotopic carbon in, respectively, the carbonyl and carboxyl groups, and from the proportions of isotopic carbon present (compared with that calculated on the basis of random condensation of C_2 units with either ordinary or isotopic carbon present in the carboxyl groups) it was concluded that the original acid had been converted to ketone compounds mainly by fission into C_2 chains with subsequent recondensation of the latter, and to a lesser extent by direct β-oxidation. All of the excess ^{13}C in the carbon dioxide produced could be accounted for as the result of the decarboxylation of keto-acids, and did not necessarily represent a different oxidation course in the breakdown of the original fatty acid.

On the simple β-oxidation hypothesis, the acetone and acetoacetic acid produced would contain no carbon isotope :

$$\begin{array}{l}\mathrm{CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.{}^{13}COOH}\rightarrow\\ \mathrm{CH_3.CO.CH_2.COOH+CH_3.COOH+CH_3.{}^{13}COOH.}\end{array}$$

On the multiple alternate oxidation view, some of the acetoacetic acid, but none of the acetone, might be expected to contain isotopic carbon :

$$\begin{array}{l}\mathrm{CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.{}^{13}COOH}\rightarrow\\ \mathrm{CH_3.CO.CH_2.CO.CH_2.CO.CH_2.{}^{13}COOH}\rightarrow\\ \mathrm{CH_3.CO.CH_2.COOH+CH_3.CO.CH_2.{}^{13}COOH}\\ \qquad\quad\downarrow\qquad\qquad\qquad\qquad\quad\downarrow\\ \mathrm{CH_3.CO.CH_3+CO_2}\qquad\mathrm{CH_3.CO.CH_3+{}^{13}CO_2}\end{array}$$

On the β-oxidation-condensation hypothesis, isotopic carbon would be present both in some of the acetone and some of the acetoacetic acid :

$$\begin{array}{l}\mathrm{CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.{}^{13}COOH}\rightarrow\\ \mathrm{CH_3.COOH+CH_3.COOH+CH_3.COOH+CH_3.{}^{13}COOH}\\ \left\{\begin{array}{lll}\mathrm{CH_3.COOH+CH_3.COOH} & \rightarrow\mathrm{CH_3.CO.COOH} & \rightarrow\mathrm{CH_3.CO.CH_3+CO_2}\\ \mathrm{CH_3.{}^{13}COOH+CH_3.COOH} & \rightarrow\mathrm{CH_3.{}^{13}CO.CH_2.COOH} & \rightarrow\mathrm{CH_3.{}^{13}CO.CH_3+CO_2}\\ \mathrm{CH_3.COOH+CH_3.{}^{13}COOH} & \rightarrow\mathrm{CH_3.CO.CH_2.{}^{13}COOH} & \rightarrow\mathrm{CH_3.CO.CH_3.+{}^{13}CO_2}\\ \mathrm{CH_3.{}^{13}COOH+CH_3.{}^{13}COOH} & \rightarrow\mathrm{CH_3.{}^{13}CO.CH_2.{}^{13}COOH} & \rightarrow\mathrm{CH_3.{}^{13}CO.CH_3+{}^{13}CO_2}\end{array}\right.\end{array}$$

As stated, the experimental findings of Weinhouse and his co-workers definitely support the β-oxidation-condensation hypothesis.

Verkade, Lee, and co-workers [111] have shown that another type of oxidation may also occur, termed ω-oxidation, i.e. conversion of the terminal methyl group into a carboxylic acid. When some of the triglycerides of the lower fatty acids (C_8–C_{11}) are ingested, the dicarboxylic acids corresponding to these fatty acids are excreted in some quantity. In other cases the dicarboxylic acids do not appear as such ; Verkade believes that this is not because ω-oxidation is uncommon, but because ω-oxidation of the acids with longer chains is accompanied by biterminal (or bilateral) β-oxidation of the dicarboxylic acids which are primarily formed. Kuhn and Köhler [112] have shown that polyene acids also undergo ω-oxidation : by feeding sorbic acid, $\mathrm{CH_3.CH{:}CH.CH{:}CH.COOH}$, they obtained muconic acid, $\mathrm{COOH.CH{:}CH.CH{:}CH.COOH}$. According to Verkade, all normal saturated dicarboxylic acids are subject to biterminal β-oxidation, and Artom [113] also considers that simultaneous β-oxidation at both ends of the molecules is involved during the biological oxidation of dicarboxylic acids. Bernhard,[114] however, from the result of studies of administration of deuterised adipic, suberic, azelaic, and sebacic acids, found that these could readily be detected when present in the urine of dogs and rats (and are thus not further broken down by β-oxidation as supposed by Verkade). Since these acids are not present in detectable amounts as intermediate products of normal fat degradation, Bernhard therefore considers that it is only the C_8 to C_{11} fatty acids which undergo ω-oxidation in the body, and that Knoop's theory of β-oxidation is the best available explanation of the oxidation of the long-chain natural fatty acids in the animal body.

This subject obviously must be considered to be still in the debatable stage, requiring considerable further experimental study before any final and unequivocal conclusions can be reached.

CHEMICAL DETERIORATION (RANCIDITY) IN NATURAL FATS

In concluding this chapter, very brief reference will be made to the various kinds of chemical change, generically termed " rancidity," which may take place in fats after removal from the plant or animal tissues in which they occur in nature. The subject of rancidity or deterioration of fats is a wide one, and a very large amount of work has been devoted to its investigation. Its adequate treatment demands, indeed, a separate monograph, and the reader who is specially interested in this field may be recommended to consult for fuller details the exhaustive monograph by Lea[115] entitled " Rancidity in Edible Fats." Here we must confine discussion of rancidity to a general statement of the chief chemical changes which may take place.

Rancidity is of various kinds, more especially simple hydrolysis of the glycerides into free fatty acids (and glycerol or mono- or di-glycerides), oxidation of fatty acids with production of ketones (β-oxidation), or oxidation at the double bonds of unsaturated neutral glycerides or fatty acids. The two first-named are almost exclusively the result of enzyme action; the last may proceed, indeed it usually does, by exposure to oxygen (air) alone, but it may also be influenced by the presence of enzymes and by other conditions.

(i) *Hydrolytic rancidity*

This is caused by exposure of fats to moisture in presence of lipolytic enzymes. In seeds, as we have already seen, lipase is always present and is, indeed, doubtless essential to the production of the mature, nearly neutral glycerides in the ripening seed. Consequently, seed fats are very prone to develop free fatty acid if they are kept under damp conditions. Similarly, fruit-flesh fats such as palm or olive oil very rapidly undergo partial hydrolysis unless all the non-fatty pulp is carefully removed or the material is heated with steam in order to destroy all enzymes.

On the other hand, the adipose tissue fats of animals are usually not quite so liable to become hydrolysed. The lipase content of adipose tissues is probably relatively small and, if the theory of reserve fat deposition suggested on pp. 354, 355 of this chapter holds, it is unlikely that esterification of fatty acids by lipase goes on in the adipose tissues themselves. Hydrolytic rancidity of such fats, when it occurs, is usually due to the growth of moulds (*Penicillium*, *Aspergillus*, etc., etc.) on the surface of the fat; such organisms contain lipolytic enzymes in abundance.

In the marine animal oils, again, especially liver oils and the lower-grade whale oils which are derived in part from the gut or offal of the animal, there is risk of contamination with intestinal bacteria, some of which are rich in lipase of great potency. Marine animal oils derived from intestinal sources are therefore liable to undergo hydrolysis on standing with relatively great rapidity unless the lipase has been effectively destroyed by heating with steam during the extraction of the oil.

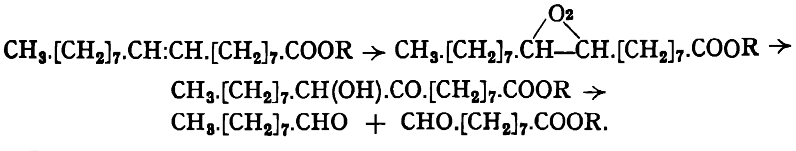
(ii) *Oxidative rancidity*

(*a*) **Ketone formation (β-oxidation).** This is not so common a form of oxidative rancidity as direct attack by oxygen at the double bonds of unsaturated glycerides, but it may be considered first, since it, like hydrolytic rancidity, is essentially an enzymic process. Further, whilst the more usual type of oxidative rancidity only affects unsaturated fats, this "ketone rancidity" involves the β-oxidation of saturated fatty acids. It is most frequently met with in coconut and palm kernel fats, but its occurrence is not entirely restricted to the nut fats. The action is due apparently to a peroxidase present in certain moulds (e.g. *Penicillium glaucum*), and these are frequently introduced into the fats from the wood of the casks in which they are stored. At moderately warm (summer) temperatures and in presence of traces of moisture and in absence of light the oxidising enzymes present attack the saturated fatty acids (those of intermediate (C_8—C_{12}) molecular weight with especial readiness) and convert them into methyl-ketones by the β-oxidation process[116]:

$$R.CH_2.CH_2.COOH \rightarrow R.CH(OH).CH_2.COOH \rightarrow R.CO.CH_2.COOH \rightarrow R.CO.CH_3.$$

By this means lauric, capric, and caprylic acids yield respectively methyl-*n*-undecyl, methyl-*n*-nonyl, and methyl-*n*-heptyl ketones, all of which possess strongly marked, heavy "perfume" odours which have caused this type of rancidity to be termed "perfume rancidity" by technologists.

(*b*) **Oxidation of unsaturated glycerides.** This is probably the most common form of rancidity and is that which is usually meant when references are made to the "rancid" flavour of an edible fat. The first products of oxidation of unsaturated fats exposed to air consist of more or less labile peroxides, which are capable of liberating iodine from a solution of hydrogen iodide in glacial acetic acid. Until comparatively recently it was commonly supposed that these peroxides result from union of oxygen with an ethenoid group, and that they alter further into keto-hydroxylic derivatives of the general type $—CH_2.CH(OH).CO.CH_2—$, which may either polymerise or, to a subordinate extent, undergo disruption with the formation of aldehydic compounds; for example:



$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.COOR \rightarrow CH_3.[CH_2]_7.\overset{O_2}{\overbrace{CH—CH}}.[CH_2]_7.COOR \rightarrow$$
$$CH_3.[CH_2]_7.CH(OH).CO.[CH_2]_7.COOR \rightarrow$$
$$CH_3.[CH_2]_7.CHO + CHO.[CH_2]_7.COOR.$$

In the atmospheric oxidation of conjugated unsaturated fatty compounds at the ordinary temperature, and (to some degree) of oleic or linoleic compounds at more elevated temperatures (e.g. 100° C.), evidence has been given that the oxidation takes this course, and in the case of elaeostearic esters hydroxyketonic derivatives of the type illustrated have been shown to be produced (Morrell *et al.*[117]).

Atmospheric oxidation of oleic, linoleic or linolenic glycerides at the ordinary temperature or up to about 50° C. is, however, now recognised to commence to a very large degree by the formation of a hydroperoxide group $—CH(O.OH).CH{:}CH—$.

This was first demonstrated by Farmer[118a] and co-workers in the case of isoprene derivatives related to rubber, and later[118b] with methyl oleate, linolenate, and docosahexaenoate. Further, it was shown that atmospheric oxidation of polyethenoid non-conjugated systems such as those of linoleates or linolenates was accompanied throughout by the formation of some proportion of conjugated di- and (to a less extent) tri-ethenoid compounds.[118b, c]

Farmer suggests that in the initial stages of autoxidation a hydrogen atom is dissociated from the —CH_2— group which is being attacked; with a poly-ethenoid system dissociation of a hydrogen atom from a —CH_2— group between two ethenoid groups leaves an intermediate system —CH:CH.$\dot{\text{C}}$H.CH:CH—, which is capable of resonance and may transform into the phase —CH:CH.CH:CH.$\dot{\text{C}}$H—. The production of polymerised products during autoxidation of unsaturated fatty oils may, indeed, be due to the polymerisation of conjugated unsaturated forms produced as shown during the initial formation of hydroperoxides.

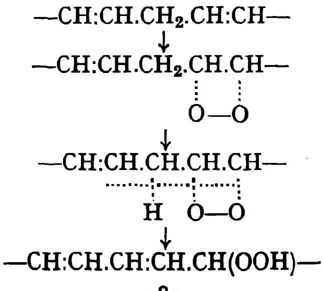
A methylene group situated between two ethenoid groups is very much more reactive to oxygen than one adjacent to only one double bond (—CH_2.CH_2.CH_2.CH:CH—), so that in di- or tri-ethenoid fatty compounds the former is almost exclusively attacked during atmospheric oxidation. Thus methyl linoleate absorbs oxygen about twelve times as rapidly as methyl oleate, whilst the rate of oxidation of methyl linolenate is only about twice that of methyl linoleate.[118e]

In Farmer's view [118b] autoxidation of the group —CH_2.CH:CH— is dependent on direct union of oxygen with the reactive —CH_2— group, no interaction of oxygen and the ethenoid bond being postulated:

$$\text{—CH}_2\text{.CH:CH—} \rightarrow \text{—CH(O.OH).CH:CH—.}$$

This mechanism was put forward because mild reduction of methyl oleate hydroperoxide gave methyl hydroxyoleate (or a mixture of hydroxyoleates) and more energetic hydrogenation gave a mixture of hydroxystearates (in which the positions of the hydroxyl groups could not be given).

Later, Bergström [118d] showed that hydrogenation of methyl linoleate hydroperoxide gave a mixture of 9- and 13-monohydroxystearic acids, and concluded that addition of oxygen formed a hydroperoxide (as envisaged by Farmer) at the reactive methylene group at C_{11}, which rapidly rearranged to a mixture of 9-hydroperoxido-$\Delta^{10,12}$-octadecadienoate and 13-hydroperoxido-$\Delta^{9,11}$-octadecadienoate. Subsequently, it has been considered by Hilditch [118e] more logical to suppose that oxygen initially associates, after all, with an ethenoid bond. The loose attachment so produced causes electronic displacements in the system —CH_2.CH:CH— (and still more so in the diethenoid system —CH:CH.CH_2.CH:CH—) which tend to liberate one of the hydrogen atoms (or rather protons) of the —CH_2— group and produce the system which exhibits resonance. Moreover, as indicated in the scheme below, this view accounts both for the apparent shifting or isomerisation of a "double bond," and for the 9- and 13-hydroxystearic acids obtained by Bergström from autoxidised methyl linoleate:



$$\begin{array}{c} \text{—CH:CH.CH}_2\text{.CH:CH—} \\ \downarrow \\ \text{—CH:CH.}\dot{\text{C}}\text{H}_2\text{.CH.CH—} \\ \vdots \quad \vdots \\ \text{O—O} \\ \downarrow \\ \text{—CH:CH.}\dot{\text{C}}\text{H.CH.CH—} \\ \text{H} \quad \text{O—O} \\ \downarrow \\ \text{—CH:CH.CH:}\dot{\text{C}}\text{H.CH(OOH)—} \end{array}$$

On this view, autoxidation of Δ^9-octadecenoic acid or esters would lead to a mixture of 9-hydroperoxido-Δ^{10}-octadecenoic and 10-hydroperoxido-Δ^8-octadecenoic acids, and not a mixture of 8- and 11-hydroperoxido-Δ^9-octadecenoic acids as suggested by Farmer.

The older chemical tests for rancidity were directed to the detection of the ultimate aldehydic products; for example, Issoglio[119a] shook the fat with distilled water and determined the amount of potassium permanganate required to oxidise the water-soluble aldehydes, and Kreis[119b] shook a dilute ethereal solution of phloroglucinol with the fat in presence of hydrochloric acid, the intensity of the pink colour produced being a measure of the amount of aldehydes present, and thus of the degree of rancidity of the fat.

Some of the more recent methods are better adapted to show the capacity of a particular sample of fat to develop rancidity. Different fats (even of the same kind, e.g. tallows or lards) possess widely varying powers of resistance to attack by atmospheric oxygen, and it is clearly more important, from a practical standpoint, to know how quickly an edible fat will develop rancidity than to determine how far it may eventually have become rancid.

Quantitative measurements of the iodine liberated from solutions of hydrogen iodide in acetic acid by the "peroxide oxygen" of a fat have been devised by Taffel and Revis[120a] and by Lea[120b] as a guide to the incipient rancidity of various fats. For the same purpose Chapman and McFarlane[121] have employed the oxidation of ferrous to ferric ion by the organic peroxides present, using colorimetric measurement of the ferric thiocyanate produced. Lea[122] has also pointed out that, while fats remain but little attacked by oxygen for different periods and then proceed to take up oxygen relatively rapidly, the initial "induction period" of relative stability to oxygen can be much shortened by exposure to light; further, that by exposing fats to light under standardised conditions the diminution of the induction period is proportional for different samples of fat, so that by this means fairly accurate forecasts can be made of the time during which a fat will remain in good condition under normal conditions of storage.

Highly refined fats or distilled fatty acids and esters commence to absorb atmospheric oxygen almost immediately on exposure thereto, whereas natural fats may, and frequently do, exhibit an "induction period" of varying duration before combination with atmospheric oxygen commences to set in to a measurable extent. It is, indeed, known that resistance to atmospheric oxidation is conferred upon natural fats by the presence therein of small amounts of non-fatty compounds (the precise chemical nature of which is still not well recognised) which prevent oxidation of unsaturated glycerides until they themselves have first been destroyed. Such compounds were termed "antioxygens" by Moureu and co-workers,[123] who showed that the addition of minute quantities of compounds such as hydroquinone or naphthol to fats also rendered them resistant to oxidative rancidity. Two points have become fairly clear in regard to the natural antioxygenic substances present in fats: (i) with very few exceptions the only substances which have this action on fats are *o*- or *p*- di- or poly-phenolic derivatives or compounds with similar electronic configuration; (ii) the action of such compounds is often reinforced by other substances, notably certain hydroxy-acids including phosphoric acid. The natural inhibitors of oxidation (i) include tocopherols, chromane-5,6-quinols, other complex polyphenolic derivatives including some containing basic oxygen or nitrogen, gallic acid and esters, flavone derivatives, ascorbic acid, etc. Mattill[124] distinguishes the true antioxygenic compounds of type (i), as inhibitors or antioxidants, from the reinforcing acidic compounds of type (ii) which are better termed "synergists."

In addition to the protective action of natural antioxygenic compounds, it is also known that the presence of excess of moisture in fats retards oxidative rancidity, whilst it has also been stated that the presence of free fatty acidity conduces to the onset of oxidation. In most respects, however, it should be clear from what has been said that hydrolytic and oxidative rancidity are different effects resulting from different causes and, while both may be encountered in the same fat, it does not necessarily follow that the development of free fatty acid is by any means always accompanied by oxidation, or conversely.

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CHAPTER IX

CONSTITUTION OF INDIVIDUAL NATURAL FATTY ACIDS

THIS chapter and the next deal with the constitution and significant properties of the individual fatty acids or alcohols which are the more important acyl units from which the natural triglycerides, phosphatides, or wax esters are elaborated.

The present chapter is devoted to the naturally occurring saturated and unsaturated fatty acids. Chapter X includes, firstly, a short section devoted to the synthesis of mixed triglycerides of known configuration—the aspect of synthesised triglycerides which is of growing importance in ascertaining the configuration of the corresponding natural products ; and, subsequently, sections dealing with the naturally occurring higher aliphatic alcohols (saturated and unsaturated), and the higher acyl glycerol ethers.

NATURALLY OCCURRING SATURATED FATTY ACIDS

The constitution of the normal saturated aliphatic acids up to and including *n*-hexacosanoic acid, $C_{26}H_{52}O_2$, has been formally established either by synthesis or by degradation to an acid or alcohol of known structure. The lower members of the series (up to *n*-heptanoic acid) were synthesised at various times by means of the Frankland-Kolbe sequence of reactions :

$$R.OH \rightarrow R.Cl \rightarrow R.CN \rightarrow R.COOH.$$[1]

From *n*-heptanoic acid to *n*-octadecanoic acid the proof of the straight-chain structure rested in most cases on the degradation of a higher to a lower acid by the Hofmann [2] sequence of reactions :

$$R.CH_2.COOH \rightarrow R.CH_2.CONH_2 \rightarrow R.CH_2.NH_2 \rightarrow R.CN \rightarrow R.COOH ;$$

and also by oxidising the methyl alkyl ketones (prepared from a mixture of the calcium salt of a higher fatty acid and calcium acetate) with chromic acid, when the following changes occur :

$$R.CH_2.COOH \rightarrow R.CH_2.COCH_3 \rightarrow R.COOH.$$

By the use of one or both of these processes Krafft [3] and other workers at different times demonstrated the conversion of stearic acid into heptadecanoic acid and the latter into palmitic acid, and so on, progressively down the series to *n*-nonanoic (pelargonic) acid. The latter acid was in the meantime prepared synthetically by Jourdan [4] from *n*-heptyl alcohol.

Thus, many years ago, the structure of the normal saturated fatty acids up to and including *n*-nonanoic acid, $C_9H_{18}O_2$, was established synthetically, whilst that of each of the higher members from *n*-decanoic acid to *n*-octadecanoic (stearic acid) followed from the stepwise degradation of the latter acid, losing one carbon atom at a time, and eventually reaching *n*-nonanoic acid. The similar proof of the constitution of each of the acids from *n*-octadecanoic acid to *n*-hexacosanoic acid was given in 1924 by Levene and Taylor.[5] These workers prepared *n*-octadecanoic acid by hydrogenation of oleic acid (*cf.* below) and proceeded to build up the higher acids as far as *n*-docosanoic acid by means of the sequence

$$R.COOEt \rightarrow R.CH_2OH \rightarrow R.CH_2I \rightarrow R.CH_2CN \rightarrow R.CH_2.COOH\,;$$

the reduction of the esters to corresponding higher aliphatic alcohols was effected by the method of Bouveault and Blanc.[6] Hydrogenation of erucic acid (*cf.* below) furnished behenic acid identical with the synthetic *n*-docosanoic acid, and this material was the starting point for the similar synthesis of the acids up to and including *n*-hexacosanoic acid.

Some of the foregoing syntheses of lower saturated acids were confirmed subsequently by others involving an aldol condensation. Thus, condensation of acetaldehyde yields crotonaldehyde, $CH_3.CH{:}CH.CHO$, which is converted by hydrogenation into *n*-butyraldehyde, $CH_3.CH_2.CH_2.CHO$, and this yields *n*-butyric acid on oxidation. *n*-Hexanoic acid can be produced by a similar sequence of reactions commencing with the condensation of *n*-butyraldehyde with acetaldehyde. Similar syntheses of the higher saturated acids were carried out in 1936 by reduction of higher polyene aldehydes produced by repeated condensation of crotonaldehyde; and it was not until this date that direct, complete syntheses of the most abundant natural higher members, such as palmitic and stearic acids, were achieved. Kuhn, Grundmann, and Trischmann[7] showed that crotonaldehyde solutions, in presence of weak salts such as piperidine acetate, undergo polymerisation into octatrienal, $CH_3.[CH{:}CH]_3.CHO$, dodecapentaenal, $CH_3.[CH{:}CH]_5.CHO$, and hexadecaheptaenal, $CH_3.[CH{:}CH]_7.CHO$. Reduction of the latter C_{16} polyene aldehyde gave cetyl alcohol, whilst hydrogenation of its condensation product with malonic acid, followed by distillation, yielded stearic acid. F. G. Fischer, Hultzsch, and Flaig[8] also obtained octatrienal and dodecapentaenal by a similar process, and converted the latter into lauraldehyde by reduction, and also, by condensation with malonic acid, into tetradecahexaenoic acid, $CH_3.[CH{:}CH]_6.COOH$. Later, Schmitt and Obermeit[245] condensed sorbaldehyde (1 mol.) with crotonaldehyde (2 mols.) in presence of piperidine acetate and obtained tetradecahexaenal, which was converted into palmitic acid by condensation with malonic acid, decarboxylation, and hydrogenation; crotonaldehyde and dodecapentaenal in presence of piperidine acetate gave hexadecaheptaenal with some eicosanonaenal, $CH_3.[CH{:}CH]_9.CHO$.

In his Pedler lecture[9] to the Chemical Society, R. Kuhn has discussed these interesting syntheses, with special reference to the part which similar reactions may play in the elaboration of the higher fatty acids in nature; he points out that, if polyene aldehyde formation is an integral part of the process, reduction of these substances must set in at an early stage, because no sign of their presence has been observed in, for example, ripening seeds.

The melting points of the saturated fatty acids alternate according as the molecule contains an even or odd number of carbon atoms; the melting points of the two series lie on two smooth curves which gradually approach one another with increasing molecular weight. Similar regularities hold in the case of the methyl and ethyl esters of the fatty acids. Owing to the marked tendency of closely related members in the higher fatty acid series to form solid solutions or molecular compounds, great care has to be taken in the interpretation of the observed melting point of any specimen. Thus, it may happen that a specimen possesses an apparent melting point practically identical with that of an individual acid, and may nevertheless be a mixture of two or even three fatty acids. For acids of molecular weight up to and including palmitic, or perhaps stearic, acid the behaviour on admixture of the specimen with a known fatty acid usually affords some indication as to its individuality. No depression in melting point is obtained when the specimen under examination is identical with the individual acid with which it is mixed, whilst, if the specimen is a mixture of two acids, admixture with a third individual acid usually depresses the melting point; but admixture with a specimen of either of the acids actually present may either raise or depress the observed melting point, in which case the evidence is inconclusive. These rules are, however, by no means generally observed, and the identification of a saturated fatty acid by means of melting point and mixed melting point determinations is a matter of some difficulty. Indeed, with the higher acids no reliance can be placed on observations of melting point. Thus whilst *n*-eicosanoic acid, $C_{20}H_{40}O_2$, melts at 75·4° and *n*-docosanoic acid, $C_{22}H_{44}O_2$, at 80·0°, Francis, Piper, and Malkin [10] have shown that certain mixtures of the following acids all melt between the limits 74·9° and 75·2°:

$$C_{20}+C_{21},\ C_{21}+C_{22},\ C_{22}+C_{23},\ \text{and}\ C_{22}+C_{23}+C_{24}.$$

Considerable attention has been given in the past few years to the study of the X-ray spectra of solid crystals of the higher saturated fatty acids, and it appears that characteristic X-ray spacings are readily obtained in the case of individual acids. The earlier work on this subject was due to Müller and Shearer [11] and it has been developed by Piper, Malkin, and Austin [12] and by Morgan and Holmes.[13] Some of this work is further referred to below in connection with difficulties formerly encountered in assigning chemical structures to natural arachidic and lignoceric acids; although at one time the evidence was considered to point to the presence of branch-chain acids in certain cases, the work of Francis, Piper, and Malkin [10] led to the conclusion that the arachidic, lignoceric, cerotic, and montanic acids which they examined from various natural sources were mixtures of *n*-fatty acids and that *iso*-acids were not present. They also emphasised, as a result of examination both of pure acids and of a large number of artificial mixtures of the latter, that a normal fatty acid cannot be considered pure unless it has the correct melting point and correct acid value and gives both of two characteristic X-ray spacings.

Chibnall, Piper *et al.*[14] subsequently made a comprehensive investigation of the melting points and X-ray spectrographic data of the alcohols and acids present in a large number of plant and insect waxes. With the aid of the corresponding data for synthetic normal alcohols (and their acetates) and acids (and their ethyl esters) containing from 26 to 36 carbon atoms in the molecule, these workers showed that the natural substances known as ceryl alcohol, cerotic acid, melissyl alcohol, melissic acid, etc., etc., are invariably mixtures of several homologues.* They suggest that names of this kind should be deleted from the literature in so far as they imply a definite molecular species, and that actual compounds (e.g. *n*-$C_{26}H_{53}(OH)$ or *n*-$C_{25}H_{51}.COOH$) should only be denoted by their systematic names, e.g. *n*-hexacosanyl alcohol or *n*-hexacosanoic acid. The adoption of this sweeping recommendation would certainly effect a helpful clarification in the literature of this part of the subject.

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* The wax aliphatic acids of high molecular weight, like the glyceride fatty acids somewhat lower in the series, are confined to members which contain an even number of carbon atoms in the molecule.

It may be pointed out that, in practice, the need for the employment of X-ray methods of analysis in addition to the ordinary determination of melting point is confined to the comparatively small number of cases in which natural saturated acids containing 20 or more than 20 carbon atoms in the molecule are concerned.

Table 98 gives a summary of the chief properties of the saturated acids encountered in natural fats, together with the X-ray spacings of some of the higher members.

TABLE 98. *SATURATED FATTY ACIDS*

SYSTEMATIC NAME	COMMON NAME	FORMULA	ACID		X-RAY SPECTRA SPACINGS	
			M.P.	B.P.	B	C
n-Butanoic	Butyric	$CH_3.[CH_2]_2.CO_2H$	−8°	163°		
3-Methyl-butan-1-oic	*iso*-Valeric	$(CH_3)_2.CH.CH_2.CO_2H$	−51°	174°		
n-Hexanoic	Caproic	$CH_3.[CH_2]_4.CO_2H$	−1·5°	205°		
n-Octanoic	Caprylic	$CH_3.[CH_2]_6.CO_2H$	+16°	237°		
n-Decanoic	Capric	$CH_3.[CH_2]_8.CO_2H$	31·3°	269°		
n-Dodecanoic	Lauric	$CH_3.[CH_2]_{10}.CO_2H$	43·5°	102°/1 mm.		
n-Tetradecanoic	Myristic	$CH_3.[CH_2]_{12}.CO_2H$	54·4°	122°/1 mm.		31·6
n-Hexadecanoic	Palmitic	$CH_3.[CH_2]_{14}.CO_2H$	62·9°	139°/1 mm.	39·1	35·6
n-Octadecanoic	Stearic	$CH_3.[CH_2]_{16}.CO_2H$	69·6°	160°/1 mm.	43·8	39·8
n-Eicosanoic	Arachidic	$CH_3.[CH_2]_{18}.CO_2H$	75·4°	205°/1 mm.	48·5	44·2
n-Docosanoic	Behenic	$CH_3.[CH_2]_{20}.CO_2H$	80·0°		53·0	48·3
n-Tetracosanoic	" Lignoceric "	$CH_3.[CH_2]_{22}.CO_2H$	84·2°		57·8	52·6
n-Hexacosanoic	" Cerotic "	$CH_3.[CH_2]_{24}.CO_2H$	87·7°		62·2	56·3
n-Octacosanoic	—	$CH_3.[CH_2]_{26}.CO_2H$	90·9°		67·2	61·1
n-Triacontanoic	—	$CH_3.[CH_2]_{28}.CO_2H$	93·6°		71·4	65·2

		METHYL ESTER		ETHYL ESTER		AMIDE	ANILIDE
		M.P.	B.P.	M.P.	B.P.	M.P.	M.P.
n-Butyric	$C_4H_8O_2$	—	102°	—	120°	116°	90°
iso-Valeric	$C_5H_{10}O_2$	—	—	—	—	135°	115°
n-Hexanoic	$C_6H_{12}O_2$	—	150°	—	167°	100°	95°
n-Octanoic	$C_8H_{16}O_2$	−40°	194°	−47°	208°	110°	—
n-Decanoic	$C_{10}H_{20}O_2$	−18°	224°	—	245°	108°	—
n-Lauric	$C_{12}H_{24}O_2$	+5°	87°/1 mm.	−10°	269°	110°	—
n-Myristic	$C_{14}H_{28}O_2$	19°	111°/1 mm.	+11°	295°	102°	84°
n-Palmitic	$C_{16}H_{32}O_2$	29°	130°/1 mm.	25°	143°/3 mm.	107°	90·5°
n-Stearic	$C_{18}H_{36}O_2$	38°	154°/1 mm.	31°	152°/0·2 mm.	109°	93·5°
n-Eicosanoic	$C_{20}H_{40}O_2$	45°	180°/1 mm.	41°	177°/0·3 mm.	108°	96°
n-Docosanoic	$C_{22}H_{44}O_2$	52°	—	48°	185°/0·2 mm.	111°	102°
n-Tetracosanoic	$C_{24}H_{48}O_2$	58°	—	54°	199°/0·3 mm.	—	—
n-Hexacosanoic	$C_{26}H_{52}O_2$	63°	—	60°	—	109°	—
n-Octacosanoic	$C_{28}H_{56}O_2$	67°	—	65°	—	—	—
n-Triacontanoic	$C_{30}H_{60}O_2$	71°	—	68°	—	—	—

Some notes may be added with reference to the individual saturated acids.

n-*Butyric acid*.—Although butyric acid is a natural product of the fermentation of glucose and other carbohydrates when these are acted upon by specific enzymes, its occurrence as a component of fats is confined to the milk fats of the mammalia in which it is frequently present, although not in great amount. With caproic and capric acids (*cf.* below) it was first reported as a component of butter fat by Chevreul.[15]

iso-*Valeric acid* is a striking exception to the general rules that the natural fatty acids contain an even number, and also an unbranched chain, of carbon atoms in the molecule. Its occurrence, however, is restricted to the fatty oils of the dolphin and porpoise and possibly other members of the family Delphinidæ of the marine mammalia; it has been reported to form as much as 60 per cent. of the mixed fatty acids of the head or jaw oils of the dolphin, in which it was first discovered by Chevreul [15] in 1817. Chevreul termed the acid " phocenic acid " but it was later shown that this acid was apparently the same as valeric acid, although at different times there has been some uncertainty as to whether the natural acid of dolphin or porpoise oil was the *n*- or the *iso*-form of this acid. It has also been suggested, at different times, that the acid was an equimolecular mixture of butyric and caproic acids, but the work of Klein and Stigol [16] on Black Sea dolphin oil and of Gill and Tucker [17] on porpoise jaw oil (Cape Hatteras) has established clearly that the compound present is *iso*valeric acid. The fact that the carbon skeleton of this acid is the same as that of isoprene may, of course, be purely coincidence; or, on the other hand, it may be an indication that this acid is derived from a precursor belonging to the terpene series.

n-*Caproic* (n-*hexanoic*) *acid* accompanies butyric acid in milk fats, and also occurs in very minute quantities in coconut fat and probably also in other seed fats of the Palmæ.

n-*Caprylic* (n-*octanoic*) *acid* also occurs in milk fats [18] in very small quantities and, to a larger extent (usually 6–8 per cent. of the mixed fatty acids) in coconut [19] and other kernel fats of the palm family. Its occurrence, except perhaps as a product of oxidation or other decomposition, in natural fats appears to be confined to the milk fats and the seed fats of the Palmæ.

n-*Capric* (n-*decanoic*) *acid* almost always accompanies caprylic acid in the two groups of natural fats in which the latter occurs, and is usually found in amounts of about the same respective order as the latter acid. In addition it has been observed in small quantities (ca. 3·5 per cent.) in the mixed fatty acids of the head oil of the sperm whale,[20] and in quantity in the seed fats of the elm [21] and a few other plants.

Lauric (n-*dodecanoic*) *acid* was apparently first discovered in 1842 by Marsson [22] in the fat of laurel kernels (*Laurus nobilis*); subsequently it was reported in coconut oil by Görgey.[23] It takes its name from the Lauraceæ or laurel family in which it was first observed, and in the seed fats of this family it sometimes forms a very large proportion of the mixed fatty acids, whilst it is also the most prominent acid in the seed fats of the Palmæ (usually forming 45–50 per cent. of the component fatty acids). It is occasionally found as a major or minor component of the seed fats of some other tropical plant families. In the animal kingdom it occurs in small amounts (usually about 4–8 per cent.) in butter and other milk fats, but only rarely as a component of depot fats (in a few aquatic animals).

Myristic (n-*tetradecanoic*) *acid* was first isolated in 1841 by Playfair [24] who found that it was an important constituent of nutmeg butter, the seed fat of *Myristica fragrans*. Later it appeared that the acid is present in very large proportions (frequently 75 per cent. or more) in the mixed fatty acids of other members of the Myristicaceæ, but it does not seem to be the most prominent component of any other natural fat so far investigated, with the possible exception of certain species of *Irvingia* (Simarubaceæ). At the same time, it is found in some quantity in a number of other seed fats, especially in those of the Palmæ (where it usually forms about 20 per cent. of the mixed fatty acids). On the other hand, there are very few natural fats, vegetable or animal (including marine animal), in which it is not present, although usually in amounts of the order of 1–5 per cent. of the total fatty acids; in milk fats the proportion is usually about 8–10 per cent. of the mixed fatty acids, and in the head oil of the sperm whale about 14 per cent. It is thus a widely distributed component of natural fats, but a major component in only a few biological families.

Palmitic (n-*hexadecanoic*) *acid* is *the characteristic saturated fatty acid of natural fats*, since it has been reported in practically every instance so far encountered. It was doubtless obtained by Chevreul in his researches on butters and tallows, but was first definitely characterised by Fremy,[25] who prepared it in the pure state in 1840 from palm oil, from which he named it. In many fats it is only a minor component and may form as little as 2–3 per cent. of the component fatty acids; in other cases the amount is somewhat larger and frequently amounts to about 10 per cent. of the whole whilst, again, there are well defined groups of vegetable and animal fats in which palmitic acid is definitely a major component. Amongst the latter may be mentioned a number of seed fats, of which cottonseed oil and the botanically related kapok seed oil are typical; in these, palmitic acid forms about 20 per cent. of the mixed fatty acids. Again, the important fruit-flesh fat of *Elæis guineensis*, palm oil, contains from 35 to 40 per cent. of its mixed fatty acids in the form of palmitic acid, whilst the proportion is even higher (60–70 per cent.) in the case of another fruit-flesh fat, Chinese vegetable or Stillingia tallow. As a rule, palmitic acid also forms about 25 per cent. of the mixed fatty acids of butter fats and somewhat more (about 30 per cent.) of those of the reserve or body fats of domestic animals such as cattle, sheep, and pigs. Important natural fats in which palmitic acid amounts to about 10 per cent. of the total fatty acids include olive, groundnut, soya bean, and maize oils, and also most of the fish and whale oils.

Stearic (n-*octadecanoic*) *acid* was described about 1820 by Chevreul [15] in the course of his researches on fats and, as is well known, it is a prominent component of most body fats of domestic and other animals; the amount varies under different conditions but as a rule it forms from 10 to 30 per cent. of the mixed fatty acids of such materials as lard or tallows. In milk fats the amount is somewhat smaller and may lie between about 5 and 15 per cent. Although stearic acid is thus a familiar component of many common animal fats, and although it is present, like myristic acid, in small amounts in a fairly large number of other natural fats, it is by no means so universally distributed as palmitic acid. In the vegetable kingdom it only forms a very small percentage of the mixed fatty acids of any fruit-flesh fat and does not occur in quantity in seed fats except in those of a few tropical families (notably Guttiferæ, Sapotaceæ, Dipterocarpaceæ, and Sterculiaceæ); the most familiar examples of seed fats in which stearic acid is contained in quantity are cacao butter, Borneo tallow, and shea butter. In the marine oils it is only present in very small quantities, varying from a trace to about 1 per cent. of the total fatty acids.

" Margaric " and " daturic " acids.—It may be recalled here that *n*-heptadecanoic acid, $C_{17}H_{34}O_2$ (" margaric acid "), was believed formerly to be present in some quantity in tallows, goose fat, etc., but that this was shown by Heiduschka and Steinruck [26] and by Bömer and Merten [27] to consist of an equi-molecular mixture of palmitic and stearic acids. In the meantime, however, Meyer and Beer [28] had reported that an acid of the formula $C_{17}H_{34}O_2$ was present in the saturated acids of datura oil, and gave it the name " daturic acid " ; but Verkade and Coops [29] have shown that this again is simply a mixture of palmitic and stearic acids. Again, a suggestion that " margaric " or *n*-heptadecanoic acid occurs in alfalfa (*Medicago sativa*) seed fat has been shown by Schuette and Vogel [30] to be without foundation, a mixture of palmitic and stearic acids only being concerned.

Similarly, a *n*-pentadecanoic acid, $C_{15}H_{30}O_2$, formerly reported as a component of yeast fat, is probably a mixture of two or more acids.

Arachidic (n-*eicosanoic*) *acid* is somewhat widely distributed, but usually only in small traces, in many seed fats and some animal fats. It occurs in appreciable quantities in a few Leguminous seed fats such as groundnut oil (where it forms only about 3 per cent. of the total fatty acids) and in the seeds of members of the family Sapindaceæ in which it frequently forms over 20 per cent. of the mixed fatty acids.

Considerable uncertainty has been felt as to whether the arachidic acid of groundnut oil was in reality *n*-eicosanoic acid, owing to the fact that the melting point of the acid isolated from this oil (74–75° C.) was lower than that of the synthetic straight-chain product. For this reason Ehrenstein and Stuewer [31] suggested that arachidic acid of groundnut oil contained a branched chain of unknown constitution. The examination by X-ray methods of the acid by Morgan and Holmes [32] also suggested that there was some abnormality about this acid, but, on the other hand, these workers found that arachidic acid prepared by hydrogenation of C_{20} unsaturated acids isolated from whale oil gave the normal X-ray structure for *n*-eicosanoic acid, and also that the C_{20} acid present in rambutan tallow (Sapindaceæ) to the extent of 23 per cent. is *n*-eicosanoic acid.[33] To these may be added the observation of Malkin [34] that the arachidic acid present to the extent of 20 per cent.[35] in kusum oil (from the same botanical family) is clearly shown by X-ray analysis to be *n*-eicosanoic acid. Moreover, by means of a specially designed apparatus for fractional distillation in a high vacuum, Jantzen and Tiedcke [36] succeeded in fractionating a large quantity of the methyl esters of the high molecular weight acids from arachis oil and obtained definite evidence from the melting point of the separated methyl esters and direct comparison of the corresponding acids with the synthetic acids that methyl *n*-eicosanoate (m.p. 44·4–44·7°), methyl *n*-docosanoate (m.p. 52·4–52·6°), and methyl *n*-tetracosanoate (m.p. 57·8–58·0°) were present. Thus, *n*-arachidic, *n*-behenic, and *n*-lignoceric acids are all present in small quantities in the glycerides of groundnut oil and the uncertainty as to their identification was probably caused by the difficulty of separating the individual acids.

Behenic (n-*docosanoic*) *acid* was first reported as a constituent of ben oil (the seed fat of *Moringa oleifera*) by Voelcker in 1848.[37] It is possibly present in very small proportions in a number of seed fats, for example, in groundnut oil (*cf.* above) and in rape and perhaps some other Cruciferous seed oils. In none of these instances does it form more than about 1 per cent. of the mixed fatty acids of a seed fat; and it does not seem to occur in the animal kingdom, although the marine animal oils contain large quantities of unsaturated acids with the same skeleton of 22 carbon atoms in the molecule. Erucic acid, the characteristic mono-ethylenic acid of the Cruciferæ, is also related structurally to behenic acid, and any of these unsaturated acids or their esters or glycerides are readily converted by hydrogenation into behenic acid or its corresponding derivatives.

Lignoceric (n-*tetracosanoic*) *acid* is widely distributed in many seed fats but as a rule only to the extent of comparatively small traces. It also occurs in beechwood tar [38] and in brown coal tar and is also found in the animal kingdom, usually as a component of phosphatides. It appears in somewhat greater proportions in a few seed fats, notably groundnut oil [39] and some other Leguminous seed oils; in one of these, that of *Adenanthera pavonina* (belonging to the subfamily Mimosoidæ), the amount of lignoceric acid is exceptionally large, namely, 25 per cent. of the component fatty acids.[40]

Much the same discussion has ranged over the constitution of natural lignoceric acid as over that of arachidic acid; so far as the natural fats are concerned, it seems likely, as in the case of arachidic acid, that the natural lignoceric acid is *n*-tetracosanoic acid.

"*Cerotic acid*" has long been recognised as a constituent of beeswax [41] and of other plant and animal waxes; it is, in fact, the characteristic "acid" of many plant waxes.[14] Since its occurrence is for the most part confined to the waxes rather than to the fats it need not be considered in detail here; but it should also be noted that it has been found in traces in some vegetable fats. Very possibly, even here, it originates from wax esters rather than from true glycerides. As already mentioned, "cerotic acid" of waxes is now recognised to be a mixture of several *n*-aliphatic acids of the even-numbered series, and is not solely *n*-hexacosanoic acid.

Other Natural Saturated Fatty Acids

Although the saturated acids present in natural *glycerides* belong (with the solitary exception of *iso*valeric acid) to the normal aliphatic series of acids containing an even number of carbon atoms, there are certain other groups of lipids in which other saturated acids are also present. The chief of these appear to be as follows:

Waxes of certain bacilli.—The waxes present in tuberculosis and leprosy bacilli have been shown by Anderson [42] and his collaborators to contain, in addition to (usually minor) amounts of palmitic, stearic or oleic acids, a number of saturated acids with branched chains. Tuberculostearic acid, $C_{19}H_{38}O_2$, for example, was isolated by Anderson and Chargaff [43] from tubercle wax, and was later proved by Spielman [44] to be 10-methylstearic acid. From the acetone-soluble fat of *Phytomonas tumefaciens* Velick and Anderson [280] isolated an acid $C_{20}H_{40}O_2$, phytomonic acid, which they believed to be a branched-chain acid, probably 10- or 11-methylnonadecanoic acid, a homologue of tuberculostearic acid.

Similarly, phthioic acid, $C_{26}H_{52}O_2$, is a polymethylated, branched-chain fatty acid.[45] Other branched-chain acids appear to have formulæ $C_{16}H_{32}O_2$ and $C_{22}H_{44}O_2$. The branched-chain or methyl-*n*-aliphatic acids melt considerably lower than straight-chain acids of the same carbon content.

Anderson and Spielman [45] suggested that phthioic acid is a long-chain acid containing several methyl groups (branch chains), whilst Wagner-Jauregg [246] found evidence that it contains at least three substituent methyl groups. The X-ray spectrum of barium phthioate and study of mono-layers of the acid on water led Stenhagen and Ställberg [247] to formulate it provisionally as ethyl-*n*-decyl-*n*-dodecylacetic acid, and Schneider and Spielman [248] considered that the chemical evidence was mainly consistent with this view. Robinson *et al.*,[249] however, have since synthesised the latter acid and shown that it differs from phthioic acid, as also does 2-methyl-5-*n*-decyl-*n*-pentadecanoic acid, the product of another synthesis ; Robinson inclines to the original view of Spielman that phthioic acid is a polymethyl-long-chain acid, probably 3, 13, 19-trimethyltricosanoic acid.

Schneider and Spielman [248] have synthesised 2-methylstearic, 2-methyleicosanoic, 2-methyldocosanoic, 2-methyltetracosanoic and 2-methylhexacosanoic acids starting from methylmalonic ester condensed in presence of sodium *n*-butyloxide with cetyl (or the appropriate higher alkyl) iodide ; also, from do-, tetra- or hexa-decyl magnesium bromide and ethyl 10-ketoundecanoate, they obtained condensation products which, after dehydration and hydrogenation, yielded 10-methyldocosanoic, 10-methyltetracosanoic and 10-methylhexacosanoic acids. Similarly, Keil [250] synthesised, from different branched chain alkyl bromides and ethyl malonate, a number of other branched-chain acids such as 4-ethyl-*n*-octanoic, 5-ethyl-*n*-nonanoic, 6-ethyl-*n*-decanoic, and 3- and 5-methyl-*n*-dodecanoic acids ; whilst Cason [251] prepared 17-methylstearic acid by condensing 9-carbethoxynonoyl chloride with the cadmium derivative of 7-methyloctanol (through the bromide), and reducing the 17-methyl-10-ketostearic ester thus formed.

Wool wax.—Sheep's wool contains greasy matter which consists for the most part of ester-waxes in which the alcohols are a mixture of sterols (cholesterol, isocholesterol, lanosterol). The acids with which the latter are combined do not belong to the ordinary normal aliphatic series, but are mainly saturated, with melting points lower than those of the corresponding acids of the *n*-aliphatic series. Darmstädter and Lifschütz [46] observed small amounts of hydroxylated or " lactonic " acids ($C_{15}H_{30}O_3$ or $C_{16}H_{32}O_3$, $C_{30}H_{58}O_3$ or $C_{32}H_{62}O_3$, and $C_{30}H_{60}O_4$ or $C_{32}H_{64}O_4$) and large proportions of a saturated acid ($C_{26}H_{52}O_2$ or $C_{27}H_{54}O_4$, m.p. 72–73°). Abraham and Hilditch [47] supported these earlier observations, and also found evidence of the presence of other acids of the formulæ $C_{15}H_{30}O_2$ and $C_{20}H_{40}O_2$; they consider that the wool wax acids may be structurally related to or derived from the sterols with which they are combined as esters. On the other hand, Kuwata and Ishii [48] also state that wool wax acids are not normal saturated fatty acids, but report the presence of " lanomyristic " acid, $C_{14}H_{28}O_2$, m.p. 58·5–59·5°, " lanopalmitic " acid, $C_{16}H_{32}O_2$, m.p. 44·5–46°, and of traces of " lanostearic " and " lanoarachidic " acids, m.p. 54–56° and 57–58°. The chief components are, evidently, members of a series either of cyclic or of branched-chain acids, of which an acid probably containing 26 (? 25 or 27) carbon atoms is the most abundant. Weitkamp [285] made in 1945 an important contribution as the result of preliminary separation of wool fat methyl esters by adsorption on a column of adsorbent clay followed by elaborate fractional distillation. He reported four groups of acids as follows (per cent. wt.) :

n-Acids : C_{10}, C_{12}, C_{18}, C_{20}, C_{22}, traces ; C_{14}, C_{16}, 2·8 (each) ; C_{24}, C_{26}, 1 (each).

iso-Acids, $(CH_3)_2$ CH.$[CH_2]_n$.COOH : C_{10}, C_{12}, traces ; C_{14} 2·8, C_{16} 5·8, C_{18} 4·0, C_{20} 5·0, C_{22} 4·0, C_{24} 2·8, C_{26} 3·6, C_{28} 0·8.

" *anteiso* "-*d*-Acids, CHMeEt.$[CH_2]_n$.COOH : C_9, C_{11}, C_{29}, C_{31}, traces ; C_{13} 1, C_{15} 4·8, C_{17} 3·6, C_{19} 4·8, C_{21} 5·6, C_{23} 3·6, C_{25} 7·0, C_{27} 5·2.

Optically active : 2-hydroxy-*n*-tetradecanoic traces, and -*n*-hexadecanoic 4·0.

Saturated n-*dicarboxylic acids.*—The saturated normal dicarboxylic acids $C_{21}H_{42}(CO_2H)_2$, etc., present in small quantities in the fruit-coat fat (" Japan wax ") of *Rhus* species, have already been discussed in Chapter IV (p. 152).

NATURALLY OCCURRING UNSATURATED FATTY ACIDS

It seems desirable to arrange this important group in a sequence which does not strictly follow the systematic classification with which every student of formal organic chemistry is familiar. If we adhered to the conventional system in the present instance, we should commence with the mono-ethylenic acid of lowest molecular weight found in fats, namely, the decenoic acid, $C_{10}H_{18}O_2$, which occurs in exceedingly small proportions in butter. Next would come the dodecenoic acids, $C_{12}H_{22}O_2$, found in rare instances and in small amounts in a few seed fats and marine animal oils, then the slightly less rare tetradecenoic acids, and so on. After discussing these simple mono-ethylenic higher aliphatic acids we should proceed methodically to consider the corresponding natural di-, tri-, tetra-, and penta-ethylenic acids, and finally have to return to certain mono-ethylenic acids containing a hydroxyl group or a ring-system, and to a mono-acetylenic acid. Strict adherence to the formal classification would have, in the case of the natural unsaturated fatty acids, the following disadvantages :

1. It would involve consideration, at the outset, of acids which are exceedingly rare and whose constitutions, in some cases, have not been settled.

2. Oleic acid, which is the most widely distributed of all fatty acids, and also in not a few fats their major component acid, would only be discussed after several of these rarer acids. Yet, by reason of its common occurrence, ordinary oleic acid is the member of the series whose chemical properties have been most thoroughly studied, and is also the acid on which most of the special methods of constitution determination used in this series were worked out in the first instance.

3. The mono-unsaturated acids, as a group, share many characteristic properties which differentiate them sharply from the polyethylenic acids. For example, it may be said that, broadly speaking, the mono-unsaturated acids are those which determine the general properties of the so-called " non-drying oils," while the polyethylenic acids give rise to the characteristic behaviour of the " drying oil " group. This makes it inconvenient to interpose an account of the polyethylenic acids between that of the simple aliphatic mono-ethylenic acids and that of the hydroxy- and cyclic mono-ethylenic acids or the mono-acetylenic acids.

The following general scheme of treatment of the natural unsaturated acids has therefore been adopted :

1. Ordinary oleic acid, which is present in practically all natural fats and which has received more investigation than any other individual unsaturated fatty acid, is considered separately in the first place. It is not only the most important representative of the fatty acids as a whole, but is also typical of the other mono-ethylenic acids. Its isolation and properties, the methods employed to determine its chemical constitution, its stereochemical relationships and its chemical transformations are therefore dealt with at some length.

Further, some of the isomeric forms of this acid which have been produced artificially from ordinary oleic acid will be noticed before the discussion of the remaining natural mono-ethylenic acids is resumed.

2. The remaining mono-ethylenic fatty acids next receive notice. Here it is useful to bear in mind the connection between fatty acids and biological

origin which has been pointed out in earlier chapters. In the vegetable kingdom, for example, we find, in addition to rare do- and tetra-decenoic acids, hexadecenoic, oleic, petroselinic, and erucic acids, and also the hydroxy-mono-ethylenic ricinoleic acid, the cyclic mono-ethylenic hydnocarpic and chaulmoogric acids, and the mono-acetylenic tariric acid. Mono-ethylenic acids characteristic of the marine animal oils include, on the other hand, in addition to do- and tetra-decenoic acids, hexadecenoic, oleic, gadoleic, cetoleic, and selacholeic acids.

3. After completing the survey of the naturally occurring mono-ethylenic and closely related higher fatty acids, we consider the corresponding poly-ethenoid acids, namely, the di-ethylenic linoleic acid, the tri-ethylenic linolenic, elæostearic, and licanic acids, and the poly- (tetra-, penta-, or hexa-) ethylenic acids of the C_{18}, C_{20}, and C_{22} series.

4. It should further be pointed out that, as a rule, only those acids which have been entirely or comparatively well authenticated are included. There remains a number of acids, some in the saturated and more in the unsaturated series, which have been reported (often many years ago) as individuals, but whose identity is uncertain and which require further study. Some of these acids (e.g. the supposed mono-ethenoid "hypogæic," "cheiranthic," or "rapic" acids) have been shown to be non-existent; in other cases, a supposed individual acid has been found to be a mixture of already known acids (e.g. "lycopodium oleic acid," "telfairic acid," etc.).

The order of treatment of the unsaturated acids of the natural fats will therefore be as follows:

Oleic acid (cis-Δ^{9}-*octadecenoic acid*):
  Isolation and properties, chemical constitution, stereochemical configuration, chemical transformations;
  Isomeric forms of oleic acid produced by hydrogenation or other means.

Other acyclic mono-ethenoid acids:
  Decenoic (milk fats).
  Dodecenoic and tetradecenoic (vegetable and animal fats).
  Hexadecenoic (vegetable and animal fats).
  Octadecenoic: (petroselinic, vegetable fats; vaccenic, animal fats).
  Eicosenoic: (gadoleic, marine animal fats; Δ^{11}-acid, *Simmondsia* seed wax).
  Docosenoic: (erucic, vegetable fats; cetoleic, marine animal fats).
  Tetracosenoic: (selacholeic, marine animal fats).
  Hexacosenoic and tricosenoic: (ximenic, *Ximenia* seed fat).

Hydroxy-mono-ethenoid acid:
  Ricinoleic (vegetable fats).

Cyclic mono-ethenoid acids:
  Hydnocarpic, chaulmoogric, (gorlic) (vegetable fats).

Acetylenic acids:
  Tariric acid (vegetable fats).
  Ethylenic-acetylenic acid (*Onguekoa Gore* seed fat).

Polyethenoid acids with two double bonds:
  Linoleic ($\Delta^{9, 12}$-octadecadienoic) (vegetable fats).
  Other octadecadienoic acids (animal fats).

Polyethenoid acids with three or four double bonds (vegetable fats):
  Linolenic ($\Delta^{9, 12, 15}$-octadecatrienoic).
  $\Delta^{6, 9, 12}$-octadecatrienoic.
  Santalbic.
  Elæostearic ($\Delta^{9, 11, 13}$-octadecatrienoic).
  Geometrical isomerides of elæostearic acid.
  Licanic (4-keto-$\Delta^{9, 11, 13}$-octadecatrienoic).
  Parinaric ($\Delta^{9, 11, 13, 15}$-octadecatetraenoic).

Polyethenoid acids with three, four, five, or six double bonds (marine animal fats):
Hiragonic (hexadecatrienoic).
" Stearidonic " (Octadecatetraenoic).
" Arachidonic " (Eicosatetraenoic); eicosapentaenoic.
" Clupanodonic " (Docosa-penta- or -hexa-enoic).
Tetracosahexaenoic.

OLEIC ACID, *cis*-Δ^9-OCTADECENOIC ACID, $CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.CO_2H$. Oleic acid was first recognised as a constituent of several common fats by Chevreul in his *Recherches sur les corps gras* in 1815, although it was probably not prepared in the pure condition for some considerable time. (The oleic acid or " oleine " of commerce is by no means a pure acid, since it consists of the liquid portions separated by pressing a mixture of fatty acids which has been obtained by distillation in a current of superheated steam under reduced pressure; this liquid oleine will usually contain, therefore, in addition to oleic acid, any more unsaturated acids (such as linoleic) which may have distilled over without decomposition, and it will also contain in solution varying proportions of palmitic or other saturated acids which have not separated in the solid condition and remained in the residue of " stearines.")

Isolation of pure oleic acid. For the preparation of pure oleic acid it is usual to select as raw material a fatty oil of comparatively simple composition containing a high percentage of combined oleic acid (for example, olive or almond oil). Since it is more difficult to separate oleic acid quantitatively from linoleic acid than from saturated acids, it may well be preferred to commence from a fat such as ox or sheep depot fat, or from a seed fat such as cacao butter or Allanblackia fat; for, although saturated acids predominate in these materials, the oleic acid present is accompanied by only very small proportions of linoleic or other diethenoid acids. After removal of most of the saturated acids from the mixed fatty acids of such a fat by crystallising their lead salts from alcohol, the unsaturated acids may be freed from linoleic acid by crystallising the barium salts from benzene containing 5 per cent. of 95 per cent. alcohol [49] or by crystallising the lithium salts from 80 per cent. alcohol.[50] After two or three crystallisations the separated barium or lithium salts will be free from linoleates, and will yield a mixture of oleic acid with a small amount (perhaps 3–4 per cent. at most) of palmitic or other saturated acids. If this product is converted into methyl or ethyl esters and the latter are fractionally distilled in a vacuum (*cf.* Chapter XI, pp. 474–483), fractions of almost completely pure methyl or ethyl oleate may be collected which furnish pure oleic acid on hydrolysis.

Another method of isolation of pure oleic acid which has been recommended by Bertram [51] is to treat mixed fatty acids containing a high percentage of oleic acid with mercuric acetate in methyl alcohol and acetic acid, when the mercury compound of oleic acid remains in solution; after filtering, the oleic acid is regenerated from the filtrates, and further purified by crystallisation from acetone at −15° to −20° C.

Brown [52] has recently described methods whereby oleic acid can be obtained practically pure by direct crystallisation from solvents at low temperatures. For example, the acids from olive oil are first separated from saturated acids by crystallising out the latter from acetone at −20°, followed by several crystallisations of the oleic acid from about 7 per cent. solution in acetone at −60°. The yield of oleic acid, m.p. 13°, so obtained is about 50 per cent. of that present in the olive oil mixed acids. The low temperature crystallisation method can be applied equally successfully, of course, to the unsaturated acids from a solid fat such as ox or sheep tallow, cacao butter, etc.

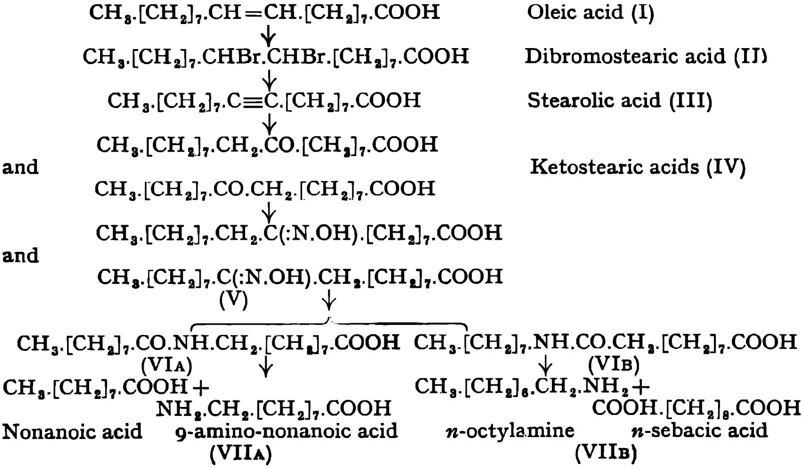
Properties of oleic acid. Oleic acid crystallises in two forms, one melting at 13° C. and the other at 16° C. It partly decomposes on distillation at atmospheric pressure, but may be distilled at reduced pressure: its boiling point is 285·5–286·0°/100 mm., 232·5°/15 mm., 153·0°/0·1 mm. The methyl and ethyl esters are colourless liquids which distil at about 150°/3 mm. or 130–135°/0·1 mm.

Wheeler and Riemenschneider [252] state that highly purified methyl oleate melts at −19·9°, oleic acid at 13·0–13·2° and 16·0–16·3°, and triolein (prepared by esterification of the latter) crystallises in three polymorphic forms, m.p. −32°, −12° and 5°.

On treatment with thionyl chloride or phosphorus chlorides, oleic acid undergoes some decomposition other than the simple formation of its acid chloride, $C_{17}H_{33}.COCl$. Oleic acid chloride, however, is produced smoothly when the acid is heated with oxalyl chloride, and the product purified by distillation in a vacuum. The same method is available for the production of the acid chlorides of elaidic, linoleic, and linolenic acids (Longenecker *et al.* [279]).

Chemical constitution of oleic acid. For a long time after Varrentrapp [53] had shown in 1840 that palmitic acid was produced in large quantities when oleic acid was fused with caustic potash, it was considered that the acid had the constitution $CH_3.[CH_2]_{14}.CH{:}CH.COOH$; but this reaction undoubtedly involves the migration of a double bond towards the carboxyl group under the influence of the molten potash. The structure at present accepted for oleic acid was first proposed by Baruch [54] in 1894, who arrived at it by means of the following somewhat complicated sequence of changes.

Oleic acid (I) was converted by bromine into dibromostearic acid (II) which, when heated with concentrated alcoholic potash lost two molecules of hydrogen bromide and produced an acetylenic acid, stearolic acid (III). When stearolic acid was treated with concentrated sulphuric acid a molecule of water was added and the ketostearic acids (IV) produced. The oximes of these acids (V) were submitted to the Beckmann rearrangement and amongst the resulting scission products Baruch was able to identify (VIIA) nonanoic acid and 9-aminononanoic acid and also (VIIB) *n*-octylamine and *n*-sebacic acid. The respective pairs of products VIIA and VIIB must have been produced by hydrolysis of the corresponding acid amido-derivatives VIA and VIB, which must accordingly have the formulæ assigned to them; consequently, the position of the unsaturated linkage in stearolic acid (and therefore in the original oleic acid) must have been between the ninth and tenth carbon atoms of the chain, counting the carboxylic carbon atom as number one.



$CH_3.[CH_2]_7.CH{=}CH.[CH_2]_7.COOH$ Oleic acid (I)

$\downarrow$

$CH_3.[CH_2]_7.CHBr.CHBr.[CH_2]_7.COOH$ Dibromostearic acid (II)

$\downarrow$

$CH_3.[CH_2]_7.C{\equiv}C.[CH_2]_7.COOH$ Stearolic acid (III)

$\downarrow$

$CH_3.[CH_2]_7.CH_2.CO.[CH_2]_7.COOH$

and Ketostearic acids (IV)

$CH_3.[CH_2]_7.CO.CH_2.[CH_2]_7.COOH$

$\downarrow$

$CH_3.[CH_2]_7.CH_2.C({:}N.OH).[CH_2]_7.COOH$

and

$CH_3.[CH_2]_7.C({:}N.OH).CH_2.[CH_2]_7.COOH$

(V) $\downarrow$

$CH_3.[CH_2]_7.CO.NH.CH_2.[CH_2]_7.COOH$ (VIA) $\downarrow$ $CH_3.[CH_2]_7.NH.CO.CH_2.[CH_2]_7.COOH$ $\downarrow$ (VIB)

$CH_3.[CH_2]_7.COOH + NH_2.CH_2.[CH_2]_7.COOH$ Nonanoic acid 9-amino-nonanoic acid (VIIA)

$CH_3.[CH_2]_6.CH_2.NH_2 + COOH.[CH_2]_8.COOH$ *n*-octylamine *n*-sebacic acid (VIIB)

Much simpler proof of the position of the double bond in oleic acid (or other unsaturated acids) has since been given by means of oxidation processes, although early attempts to oxidise oleic acid with nitric acid led to the production[55] of a mixture of monobasic and dibasic acids, the former including those from formic acid up to capric acid and the latter adipic, pimelic, and suberic acids. Similarly, aqueous acid potassium permanganate produces, in addition to dihydroxystearic acid, a mixture of mono- and di-basic acids. Nevertheless, by oxidising oleic acid with aqueous permanganate at 60° Edmed[56] (1898) was able to obtain in addition to 60 per cent. of dihydroxystearic acid, 16 per cent. of azelaic acid, 16 per cent. of oxalic acid and a small amount of *n*-nonanoic acid, thus supporting the structure assigned to oleic acid by Baruch.

The ozonisation process, or addition of ozone to an unsaturated ethylenic linkage, has given much more reliable data on the constitution of ethylenic acids than oxidation with aqueous reagents. Molinari[57] (1903) appears to have been the first to apply the ozonisation method to the case of oleic acid, although almost concurrently Harries and Thieme[58] published the results of very exhaustive work on the same method. The ozonisation procedures led, in the case of ordinary oleic acid, to the production of *n*-nonanoic and azelaic acids, together with the corresponding *n*-nonylaldehyde and azelaic acid semi-aldehyde, $COOH.[CH_2]_7.CHO$.*

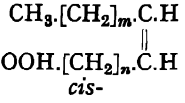
Whilst the ozonisation method thus led to satisfactory location of the double bond in oleic acid, it has sometimes the disadvantage that considerable amounts of resinous products are formed, so that the yields of the scission products obtained do not represent by any means the whole of the original unsaturated acid. Improvement in this respect was reached by Grün and Wittka[60] (1925) who obtained good yields of *n*-nonanoic and azelaic acids by oxidising stearolic acid with chromic acid ; whilst Armstrong and Hilditch[50] (1925) showed that direct oxidation of methyl or ethyl oleates with powdered potassium permanganate in hot acetone or acetic acid solution gave a mixture of nonanoic acid and methyl or ethyl hydrogen azelate :

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.COOMe \rightarrow$$
$$CH_3.[CH_2]_7.COOH + COOH.[CH_2]_7.COOMe$$

By hydrolysing the mixed acidic products of oxidation they obtained yields of 80–90 per cent. of azelaic acid and 60–70 per cent. of *n*-nonanoic acid calculated on the original ester employed.

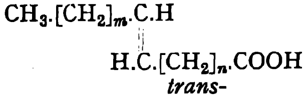
At the present time, the ozonisation method and the permanganate-acetone oxidation method appear to be most widely used for the determination of the position of the unsaturated linkages in the natural unsaturated fatty acids.

Stereochemical configuration of oleic acid. In common with all symmetrically di-substituted ethylenic compounds, it is possible for the mono-ethylenic higher fatty acids to exist in two geometrically isomeric forms which may be represented as follows:



$$\begin{array}{c} CH_3.[CH_2]_m.C.H \\ \| \\ COOH.[CH_2]_n.C.H \end{array}$$

cis-



$$\begin{array}{l} CH_3.[CH_2]_m.C.H \\ \qquad\qquad\quad \| \\ \qquad\qquad H.C.[CH_2]_n.COOH \end{array}$$

trans-

In the case of oleic acid the geometrical isomeride has not so far been found in any natural fat but it has long been known that on treatment with oxides of nitrogen, or by heating with small quantities of sulphur, oleic acid is partially transformed into an isomeric acid, elaidic acid, which still has the double bond in the 9, 10 position and is thus a geometrical isomeride of oleic acid. For many years, although the reason does not appear by any means clear, it was customary to describe oleic acid as the *trans*-isomeride. It is usual in other cases of geometrical isomerism, in the absence of any definite evidence, to regard the more stable, higher melting form as the *trans*-isomeride (in this case elaidic acid). This reasoning alone would lead us to formulate oleic and elaidic acids as follows :

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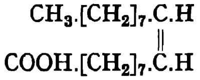
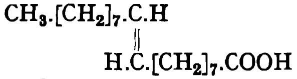
* The semi-aldehyde of azelaic acid is best prepared by the action of periodic acid on the 9, 10-dihydroxystearic acids (King[59]).



$$\begin{array}{r} CH_3.[CH_2]_7.C.H \\ \| \\ COOH.[CH_2]_7.C.H \end{array}$$

Oleic, *cis*-Δ^9-octadecenoic acid.



$$\begin{array}{l} CH_3.[CH_2]_7.C.H \\ \qquad\qquad\quad \| \\ \qquad\qquad H.C.[CH_2]_7.COOH \end{array}$$

Elaidic, *trans*-Δ^9-octadecenoic acid.

The following additional arguments, indeed, confirm this view :

(i) In 1923 Müller and Shearer [11] submitted oleic and elaidic acids, and also erucic and brassidic acids ($C_{22}H_{42}O_2$), to examination by the X-ray method of crystal analysis and deduced that the (higher melting) elaidic and brassidic acids were respectively the *trans*- forms of the respective pairs of acids. (The X-ray spectra of elaidic, erucic, and brassidic acids were re-examined in 1938 by Francis and Willis,[61] the technique of the method having naturally been developed in the fifteen years since Müller and Shearer's original study. The results, however, fully supported the conclusions drawn by the earlier investigators.)

(ii) Studies of monomolecular films on water of the same pairs of isomeric mono-ethenoid acids, and of oleyl and elaidyl alcohols, by Marsden and Rideal [62] showed that monolayers of the " elaidic " forms are less highly expanded than those of the " oleic " or natural acids, and in this respect resemble the corresponding saturated acids, whilst mixed films of an " elaidic " form with its corresponding saturated acid interlock to form " close-packed " films. Similar mixed films of an " oleic " form with its corresponding saturated acid cause expansion of the film. Moreover, monolayers of the individual " oleic " acids are not only more highly expanded than those of the corresponding " elaidic " acids, but the films collapse to form oil lenses, whereas those of " elaidic " forms interlock on compression to form solids or smectic liquids. All these observations show consistently that the natural " oleic " compounds possess the *cis*- configuration, since the *cis*-ethenoid bond leads to a deformation of the molecular chain which would give rise to the observed phenomena, whereas the *trans*-ethenoid bond produces little deformation in the chain, which remains almost exactly similar to that of the saturated acid.

Harkins and Florence,[63] supporting the conclusions of Marsden and Rideal, observe that *cis*- compounds are more readily squeezed out of monolayers than *trans*- compounds, and point out that the bend in the hydrocarbon chain at the double bond of *cis*- compounds causes the latter to be less firmly bound to other adjacent molecules than is the case with *trans*- compounds.

(iii) The fact that " elaidic " forms of the unsaturated fatty acids form solid solutions [64] with the corresponding saturated acids (e.g. elaidic with stearic, or brassidic with behenic), whilst the natural forms (e.g. oleic erucic) do not do so, is further evidence that the " elaidic " derivatives are closely related in configuration to the saturated acids, i.e. they are the *trans*-isomerides of the mono-ethenoid compounds.

(iv) Armstrong and Allan [65] pointed out that the absence of elaidic acid in nature is consistent with its being the *trans*- isomeride, since chemical changes induced by enzyme action in the living cell do not as a rule lead to the production of an isomeride of maximum stability.

(v) G. M. and R. Robinson [66] stated that the production of oleic acid from stearolic acid by zinc and hydrochloric acid in presence of titanous chloride indicates that oleic acid has the *cis*- configuration.

(vi) McCutcheon *et al.*[67a] have studied the infra-red absorption spectra of oleic, linoleic and linolenic acids, and of elaidic acid and the isomerised form of linoleic acid (m.p. 28–29°, *cf.* p. 423). The first three acids all showed strong infra-red absorption at $6{\cdot}0\mu$ (characteristic for *cis*-compounds), whilst the other two acids had much weaker absorption at $6{\cdot}0$–$6{\cdot}1\mu$ (in common with other *trans*-compounds).

The Raman spectra of oleic, ricinoleic and linoleic acids have also been examined by Dupont and Yvernault,[67b] who showed that all three acids possessed the *cis*-structure, whilst elaidic and ricinelaidic acids were each observed to have the *trans*-configuration.

Infra-red and Raman spectral analyses thus fully confirm the conclusion that oleic and the other naturally occurring unsaturated fatty acids possess the *cis*-configuration.

Interconversion of oleic and elaidic acids. The conversion of triolein into trielaidin by means of oxides of nitrogen was apparently first observed by Poutet in 1819,[68] who employed a solution of mercury in nitric acid as the source of the oxides of nitrogen. This test, known as the elaidin test, was formerly much used as a qualitative test for non-drying oils. The nature of the change was not thoroughly investigated for many years, but Jegorow [69] showed that the transformation was effected by relatively small proportions of the reagent, and that the use of larger proportions led to the production of addition products such as $C_{18}H_{34}O_2(NO_2)(NO)$ and $C_{18}H_{34}O_2(NO_2)(OH)$.

In 1894 Saytzew [70] showed that the same change takes place when oleic acid is treated with sulphurous acid or sodium bisulphite under pressure at 180–200°, whilst later Albitski [71] found that the reverse change of elaidic to oleic acid proceeded under these conditions to the extent of about 20 per cent. More recently (1929) Rankow [72] observed that small amounts of sulphur effect the partial transformation of oleic into elaidic acid at about 200°. A quantitative study of the oleic-elaidic acid transformation by means of these various reagents was undertaken in 1932 by Griffiths and Hilditch,[73] who found that the action is a balanced one and that the same equilibrium is attained commencing from either oleic or elaidic acids; in either case, using Poutet's reagent or gaseous oxides of nitrogen prepared from arsenious oxide and nitric acid, these authors found that the reaction product contained elaidic acid to the extent of about 66 per cent. of the oleic or elaidic acid originally employed, and that (depending upon the particular reagent used) varying amounts of addition products (nitrogen or sulphur compounds according to the reagent employed) were present in the final mixture. They also found that the same equilibrium point was reached when the methyl or glyceryl esters of oleic acid were submitted to the isomerisation, and that, in the similar cases of petroselinic (*cis*-Δ^6-octadecenoic) and erucic (*cis*-Δ^{13}-docosenoic) acids, the equilibrium mixture produced by isomerisation contained somewhat more than twice as much of the respective *trans*- acids as of the (original) *cis*- acids.

Probably the most efficient catalyst for elaidinisation is selenium, which Bertram[74] showed in 1936 to be effective in concentrations of 0·1–0·3 per cent. at about 180–200°. The *cis-trans* equilibrium is rapidly attained and, the proportion of selenium being so small, the presence of addition products with the catalyst, or other by-products, is minimised. Indeed, linoleic acid, which yields high proportions of by-products when treated with oxides of nitrogen or elemental sulphur as isomerising agents, can be isomerised with small proportions of selenium at 200° with little loss other than slight polymerisation (*cf.* p. 423).[75, 205]

Syntheses of Δ^{9}-octadecenoic acids. The formal synthesis of oleic acid was first attempted by G. M. and R. Robinson[66] in 1925; these workers indeed effected a complete synthesis of 10-ketostearic acid, and also showed that stearolic acid could be converted into oleic acid, but were unable to transform 10-ketostearic acid into stearolic acid. They condensed the sodium derivative of ethyl 2-acetylnonoate (I) (from *n*-heptyl iodide and acetoacetic ester) with 9-carbethoxynonanoic acid chloride (II) and obtained the ester (III), which, after successive hydrolysis with cold dilute alkali and boiling dilute sulphuric acid, gave 10-ketostearic acid (IV):

$$\begin{array}{c} \underset{\text{I}}{CH_3.[CH_2]_6.CH.(COCH_3).COOC_2H_5} + \underset{\text{II}}{Cl.CO.[CH_2]_8.COOC_2H_5} \\ \downarrow \\ \underset{\text{III}}{CH_3.[CH_2]_6.C(COCH_3)(COOC_2H_5).CO.[CH_2]_8.COOC_2H_5} \\ \downarrow \\ \underset{\text{IV}}{CH_3.[CH_2]_7.CO.[CH_2]_8.COOH} \end{array}$$

Although stearolic acid (V) can be hydrated to a mixture of 9- and 10-ketostearic acids the reverse change has not yet been accomplished; but its reduction with titanous chloride in acetic acid produced oleic acid (VI) (*cf.* p. 402):

$$\underset{\text{V}}{CH_3.[CH_2]_7.C{:}C.[CH_2]_7.COOH} \rightarrow \underset{\text{VI}}{CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.COOH}$$

It may be noted that 10-hydroxystearic acid (obtainable from 10-ketostearic acid by reduction) yields 10-iodostearic acid, which was shown many years ago by Saytzew[76] and by Arnaud and Posternak[77] to give a mixture of oleic, elaidic, and hydroxystearic acids when heated with alcoholic potash. In conjunction with Robinson's synthesis of 10-ketostearic acid, these observations therefore define oleic and elaidic acids by synthesis as either the Δ^{9}- or Δ^{10}-octadecenoic acids.

A total synthesis of Δ^{9}-octadecenoic acid, in the form of the equilibrium *cis-trans* mixture, was effected by Noller and Bannerot[78] in 1934 commencing from 9-chlorononyl aldehyde (I). This aldehyde, on treatment with bromine, hydrogen bromide, and methyl alcohol, gave 8, 9-dibromo-9-methoxynonyl chloride (II) which, submitted to the Grignard reaction with magnesium *n*-octyl bromide (III) yielded 8-bromo-9-methoxyheptadecyl chloride (IV). Reduction of the latter compound in *n*-butyl alcohol solution with zinc produced Δ^{8}-heptadecenyl chloride (V), which was converted into the corresponding cyanide (VI) and the latter hydrolysed to the corresponding Δ^9-octadecenoic acid (VII), which proved to be a mixture of 63 per cent. of elaidic acid and 37 per cent. of oleic acid :

$$CHO.[CH_2]_8.Cl \rightarrow CH(OCH_3).Br.CHBr.[CH_2]_7.Cl + Mg(.[CH_2]_7.CH_3)Br$$

I II III

$$\downarrow$$

$$CH_3.[CH_2]_7.CH(OCH_3).CHBr.[CH_2]_7.Cl$$

IV

$$\downarrow$$

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.Cl$$

V

$$\downarrow$$

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.CN$$

VI

$$\downarrow$$

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.COOH$$

VII

An alternative and more recent synthesis of oleic acid by Baudart[283a] commenced from *n*-decanaldehyde (I), which by bromination in ethyl alcohol gives 1-ethoxy-1,2-dibromo-decane (II). This was submitted to the Grignard reaction with the magnesium derivative of 1-methoxy-6-bromohexane (III), yielding the compound (IV). The latter, by a sequence of steps (V–VIII) somewhat similar to those of the Noller and Bannerot synthesis, finally gave a mixture of 65 per cent. of elaidic and 35 per cent. of oleic acids (IX) :

$$CH_3.[CH_2]_8.CHO$$

I

$$\downarrow$$

CH_2

$$CH_3.[CH_2]_7.CHBr.CHBr(OC_2H_5) + Br.Mg.CH_2.[CH_2]_4(OCH_3)$$

II $\downarrow$ III $\wedge$

$$CH_3.[CH_2]_7.CHBr.CH(OC_2H_5).CH_2.[CH_2]_4.CH_2(OCH_3)$$

IV

$$\downarrow$$

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_5.CH_2(OCH_3)$$

V

$$\downarrow$$

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_5.CH_2Br$$

VI

$$\downarrow$$

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_5.CH_2I + CHNa(COOC_2H_5)_2$$

VII

$$\downarrow$$

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_6.CH(COOH)_2$$

VIII

$$\downarrow$$

$$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.COOH$$

IX

For syntheses of analogues of oleic acid, of linoleic acid, and of acids of the chaulmoogric series, see (respectively) pp. 409, 425, and 418.

SOME CHEMICAL TRANSFORMATIONS OF OLEIC ACID

1. **Addition of halogens.** In common with all the unsaturated higher aliphatic acids, oleic acid reacts additively with halogens. With chlorine dichlorostearic acid is produced, whilst with bromine[79] oleic acid gives a dibromostearic acid, m.p. 28·5–29°, and elaidic acid an isomeric dibromostearic acid, m.p. 29–30°; mixtures of these dibromostearic acids melt at a much lower temperature,[80] and the individual acids, on debromination with zinc and alcoholic hydrochloric acid, revert exclusively to the acid from which they were prepared, oleic or elaidic respectively.[81, 75]

The debromination of bromo-addition products of the higher ethylenic acids is, indeed, a somewhat remarkable change, in that it has been shown not only in the foregoing cases but also in those of linoleic and linolenic acids (see below) that, in the regenerated ethylenic acids, the position of the double bonds is the same as in the original acid from which the bromo-derivative was prepared.

Iodine, or more frequently mixed halogens such as iodine monochloride or iodine monobromide, will also interact additively with ethylenic acids, and this reaction of course forms the basis for the estimation of the iodine value of unsaturated fatty oils and acids by such well-known methods as those of Wijs, Hanus, etc. Derivatives of the halogens, such as hypochlorous acid, also act additively towards oleic acid and in this way, for example, chlorohydroxystearic acids have been obtained by Albitski[82] from oleic and elaidic acids.

2. **The dihydroxystearic acids produced by oxidation of oleic and elaidic acids.** Oleic acid may be transformed by a variety of reagents into one of two 9, 10-dihydroxystearic acids, which melt respectively at 95° and 132°. Most of these reactions lead to the exclusive production of one or other of these acids, which are evidently stereoisomerides. Moreover, those reagents which cause the production of the acid, m.p. 95°, from oleic acid result in the formation of the acid, m.p. 132°, from elaidic acid, and conversely. It further follows, then, that the particular dihydroxystearic acid produced in any given case depends upon the geometrical configuration of the original ethylenic acid, and that (since under different conditions each acid results from one and the same geometrical isomeride—e.g. oleic acid) an inversion must take place during some of the chemical processes involved.

In the case of oleic acid, the dihydroxystearic acid m.p. 95° is obtained as a result of the following reactions:

(i) Addition of chlorine or bromine to oleic acid, followed by treatment of the product with aqueous or alcoholic alkali.[82]

(ii) Addition of hypochlorous acid to oleic acid followed by treatment of the resulting chlorohydroxystearic acid (*a*) with aqueous or alcoholic potash, or (*b*) with baryta, when an oxido-acid is formed which on further treatment with alkali or dilute sulphuric acid yields the dihydroxy acid m.p. 95°.[82]

(iii) Oxidation of oleic acid by Caro's acid[82] or by hydrogen peroxide and glacial acetic acid (peracetic acid),[83a] or by perbenzoic acid.[84] With the latter, or with peracetic acid[83b, 263b] below 25°, an oxidostearic (9, 10-epoxystearic) acid is first produced which, when its ethylene oxide ring is opened, yields the dihydroxystearic acid of melting point 95°.

The dihydroxystearic acid of m.p. 132° has been obtained from oleic acid in the following ways:

(i) Treatment of the chlorohydroxystearic acid (*cf.* above) by means of silver oxide.[82]

(ii) Oxidation of alkaline salts of oleic acid in dilute ice-cold alkaline aqueous solution by potassium permanganate.[66, 85, 86, 87]

In all cases elaidic acid has been submitted to the action of the different agents enumerated in the preceding paragraphs and it has been invariably found that the opposite form of dihydroxystearic acid results from that obtained when oleic acid is the starting material. Similar relationships have been observed, by several of the workers mentioned, in the cases of the isomeric petroselinic acids and the isomeric erucic and brassidic acids. Further, it has been observed that, in the oxidation by means of alkaline permanganate, good yields of the dihydroxy-acid are not obtained unless a large excess of alkali is employed [87] and that the yield of the dihydroxy-acid m.p. 95° produced from the more stable elaidic acid is invariably less than that of the isomeride obtained from oleic acid.[85]

It is not certain at what point the " inversion " takes place which causes the production of the two different acids from the same ethylenic acid. Lapworth and Mottram [88] and also Böeseken and Belinfante [89] have pointed out that oxidation by permanganate does not normally involve any change of configuration, although in a later communication [90] Lapworth considers that the matter cannot at present be settled. On the other hand, Hilditch and Lea [83a] have pointed out that the conditions necessary for the production of good yields of the dihydroxystearic acids during alkaline permanganate oxidation suggest that the inversion takes place during oxidation in a strongly alkaline medium.

More recently, G. King [253a] showed that either of the 9, 10-dihydroxystearic acids, m.p. 132° or 95° (as also the optically active form, m.p. 141°, of the m.p. 132° acid which occurs in small proportions in castor oil), furnish the opposite isomeride (m.p. 95° or 132° respectively) after conversion by hydrogen chloride at 160° into chlorohydrins, formation of oxidostearic acids from the latter, and subsequent opening of the oxido-ring. King concludes, in view of the fact that the optically active acid gave rise to an oxido-acid which possessed a small, but perceptible, rotatory power, that a Walden inversion takes place during hydration of the oxido-ring system. This supports the view that the dihydroxy-acid, m.p. 132°, is stereochemically related to oleic acid, and that the production of the opposite form, m.p. 95°, by oxidation of oleic acid with per-acids involves the intermediate formation of an oxido-acid which undergoes " inversion " during subsequent opening of the oxido-ring. Whilst perbenzoic acid and oleic acid yield oxidostearic acid accompanied by the dihydroxystearic acid, m.p. 95°, the oxido-acid or epoxide is not usually present in the products formed when peracetic acid or Caro's acids are the oxidising media ; but King [253b] has shown that under suitable conditions oxidostearic acid may be isolated during the oxidation of elaidic acid with peracetic acid, and its non-occurrence in normal conditions is probably due to its more complete hydrolysis *in situ* in presence of relatively strong acids such as acetic or sulphuric.

On the other hand, Atherton and Hilditch [254] have shown that either form of oxidostearic acid, on treatment with anhydrous hydrogen chloride, yields a chlorohydroxystearic acid which reverts in presence of alcoholic alkali to the same form of oxidostearic acid as that originally employed ;

this suggests that, at all events under these conditions of ring opening and closure, inversion occurs either during both closing and opening of the oxido-ring, or at neither stage. These authors therefore conclude that the inversion involved in King's sequence of actions takes place during replacement of a hydroxyl group by chlorine during the action of hydrogen chloride at 160° (when the products are chloro-estolides and not chlorohydroxystearic acids).

Meanwhile, the rotatory powers of the four active forms of 9, 10, 12-trihydroxystearic acid obtained by Kass and Radlove[255] from ricinoleic and ricinelaidic acids (*cf.* p. 416) by alkaline permanganate oxidation appear to these authors to conform with the assumption that oleic acid and the dihydroxystearic acid, m.p. 132°, are directly related; but interpretation of stereochemical configuration from the degree of rotatory power is perhaps somewhat uncertain. It must therefore be admitted that the stereochemical relationships of oleic, elaidic, and the two corresponding 9, 10-dihydroxystearic acids (and the corresponding relationships of other *cis*- and *trans*-ethenoid long-chain acids with their corresponding hydroxy-saturated acids) present a problem, of very long standing, which still awaits an unequivocal decision; but at the present time there appears on the whole to be more likelihood that the *cis*- (oleic) acids are directly related to the dihydroxy-saturated acids of higher melting-point, and conversely.

More intensive oxidation of oleic acid by dilute alkaline permanganate solutions, or further oxidation of the 9, 10-dihydroxystearic acid of m.p. 132° by the same reagent, was shown by Lapworth and Mottram[87] to lead to the production of suberic, oxalic, and *n*-octanoic acids (instead of the two C_9 acids, azelaic, and *n*-nonanoic). Green and Hilditch[91] showed that the isomeric 9, 10-dihydroxystearic acid of m.p. 95° undergoes the same decomposition, and that the same course is also followed in other dihydroxy-saturated acids, irrespective of the length of the carbon chain, the position of the double bond or its *cis*- or *trans*- configuration in the mono-ethenoid acids from which the dihydroxy-saturated acids originated. The dihydroxy-behenic acids were much less susceptible to oxidation than the dihydroxy-stearic or dihydroxypalmitic acids.

Green and Hilditch also examined the corresponding behaviour of the polyethenoid linoleic, linolenic, and elæostearic acids under similar conditions of oxidation, and found that in these cases about 80 per cent. was converted by direct scission to azelaic acid, the remaining 20 per cent. leading to suberic acid (as above). Farmer *et al.*,[92] employing faintly alkaline solutions of permanganate, have obtained only azelaic acid in the oxidation of elæostearic and other polyethenoid acids, and it may well be that the alternative course is the result of oxidation of the di-enolic form of a diketo-acid produced as an intermediate product:

$$-\mathrm{CH_2.CH(OH).CH(OH).CH_2}- \rightarrow -\mathrm{CH_2.CO.CO.CH_2}- \rightarrow$$
$$-\mathrm{CH{:}C(OH).C(OH){:}CH}-$$

The oxidation of dihydroxy-long-chain saturated acids by lead tetra-acetate (or a solution of red lead in acetic acid) results in scission into an alkylaldehyde and the semi-aldehyde of a dicarboxylic acid. Thus Hsing and Chang,[256] and Scanlan and Swern,[83b] have obtained high yields of *n*-nonaldehyde and the semi-aldehyde of azelaic acid from 9, 10-dihydroxystearic acids. Hilditch and Jasperson[257] have shown that the rates of oxidation by lead tetra-acetate of the lower melting form (95°) of 9, 10-dihydroxystearic acid, and of those of the 9, 10, 12, 13-tetrahydroxystearic acids (m.p. 144° and 136°, *cf.* p. 422) are in each case far more rapid than those of the higher melting isomers (m.p., respectively, 132°; and 162° and 172°).

Mendel and Coops [258] effect the degradation of a long-chain saturated acid to the next lower member by, for example, oxidising 2-hydroxystearic acid (from 2-bromostearic acid) with lead tetra-acetate, when heptadecanal is produced and, by passage of air through the tetra-acetate solution, is converted into *n*-heptadecanoic acid.

3. **Ketolstearic acids (9-hydroxy-10-keto- and 10-hydroxy-9-ketostearic acids).** Holde and Marcusson [93] showed in 1903 that if excess of alkali is avoided in the aqueous permanganate oxidation of oleic acid, the product formed contains for the most part hydroxyketostearic acids. King [94] found in 1936 that the best yields of the two hydroxyketostearic acids were obtained from oleic or elaidic acids by using alkali in equivalent amount to the fatty acid, and about 2 mols. of permanganate per mol. of fatty acid, with a concentration of acid not exceeding 1 gram per litre of solution, and oxidation for 8–10 minutes at 8–10° for oleic acid and 25° for elaidic acid. In this way a yield of 40–50 per cent. of the mixed 9-hydroxy-10-keto- and 10-hydroxy-9-keto-stearic acids can be obtained, from which King separated the pure acids by fractional crystallisation of their semicarbazones. The 9-hydroxy-10-keto-acid melts at 74°, and its isomeride at 75·5°. Periodic acid oxidises 9-hydroxy-10-ketostearic acid to nonanoic acid and the semi-aldehyde of azelaic acid,[95] and 10-hydroxy-9-ketostearic acid to nonylaldehyde and azelaic acid.

Morrell and Phillips [96] state that passage of gaseous oxygen through dilute alkaline solutions of the potassium salts of the acids at 18° rapidly and quantitatively decomposes them into nonanoic and azelaic acids. These authors also found that the 9-hydroxy- group can be methylated, whereas the 10-hydroxy- group of the isomeric acid resists methylation; they ascribe the difference in behaviour to differences in the polarity of the terminal groups (CH_3— and —COOH) of the acyl chain, leading to basic character in the 10-hydroxy-, and acidic character of the 9-hydroxy-, groups in the respective acids. Hilditch and Plimmer [259] showed that this oxidation of the ketolstearic acids is dependent upon the concentration of the alkali present; they consider that the ketolstearic acid is resolved into dihydroxystearic and diketostearic acids by the alkali, and that the scission products arise from oxidation of the latter acids, as well as from direct oxidation of hydroxyketostearic acid.

ISOMERIC FORMS OF OLEIC ACID PRODUCED BY HYDROGENATION OR OTHER MEANS

A number of acids of the oleic series which do not occur naturally have been obtained by various chemical reactions from the natural oleic or related acids. The chief instances may be grouped as follows:

(i) **Isomerisation of oleic acid by oxides of nitrogen, sulphur, selenium.** The interconversion of the *cis*- and *trans*- forms of the oleic acids has already been fully discussed (pp. 400–403).

(ii) **Isomeric oleic acids ("*iso*oleic acids") produced during catalytic hydrogenation.** It has been known for a long time that hydrogenation of oleic acid or an ester thereof yields not only stearic acid, but also, during the intermediate phases of the process, a certain proportion of solid oleic acids. It was shown by Moore [50] in 1919 that the chief component of these solid oleic acids is elaidic acid, but that in addition one or more *iso*oleic acids produced by migration of the double bond are present. The amount of *iso*oleic derivatives produced varies according to the conditions of hydrogenation, and is probably at a maximum when the operation is carried out at a high temperature (200° C. or above) and at atmospheric pressure in presence of a moderate concentration of powdered catalyst by the agitation process.[97] It has also been shown by Hilditch and Vidyarthi [98] (1929) that the isomeric oleic acids, in which migration of the double bond has occurred as a result of hydrogenation, are the *cis*- and *trans*- forms of acids with an ethylene linkage adjacent to the position which it originally occupied ; thus, from Δ^{9}-octadecenoic acid subordinate amounts of the Δ^{8}- and Δ^{10}-acids were identified in the products of partial hydrogenation by means of oxidation to the corresponding mono- and di-carboxylic acid scission products.

When polyethenoid derivatives such as linoleic or linolenic glycerides are selectively hydrogenated, the mono-ethenoid compounds formed are naturally not entirely the Δ^{9}-compounds. When, by saturation of the Δ^{9} or other positions by hydrogen, the remaining double bond occupies a position other than Δ^{9} in the molecule, the acid so produced is frequently a solid and may be considered as one of the " *iso*oleic acids " of hydrogenation.

(iii) **"*Iso*oleic acids" produced by steam distillation of "sulphonated" oleic acid.** When oleic acid is dissolved in concentrated sulphuric acid and the product subsequently boiled with water, a certain amount of 10-hydroxystearic acid, $CH_3.[CH_2]_7.CH(OH).[CH_2]_8.COOH$, m.p. 83–85°, is produced.[99]

If the products of the action of sulphuric acid on oleic acid are distilled in a vacuum at high temperature in a current of superheated steam the distillate contains, in addition to unchanged oleic acid and a certain amount of hydroxystearic acids, a mixture of isomeric forms of oleic acid, which have evidently been produced by elimination of the elements of water from the hydroxy-acids present.[100]

Arnaud and Posternak [77] stated that the composition of such a distillate was found by them to be about 31 per cent. ordinary Δ^{9}-oleic (or other liquid oleic) acid, 15 per cent. Δ^{9}-elaidic acid, 36 per cent. of a mixture of Δ^{8}- and Δ^{9}-elaidic acids with 18 per cent. hydroxystearic acids. Steger, van Loon *et al.*[101] recently separated the isomeric oleic acids present in commercial " oleine " produced by the " sulphonation " and distillation process by the lead salt alcohol method (*cf.* Chapter XI, p. 468) into 66 per cent. of " solid " and 34 per cent. of " liquid " acids. They showed that the former were a mixture of Δ^{8}-, Δ^{9}- and Δ^{10}-elaidic acids, whilst the " liquid " acids similarly contained Δ^{8}-, Δ^{9}- and Δ^{10}-oleic acids.

(iv) **"Synthetic" *iso*oleic acids.** Finally, it may be pointed out that the normal saturated acids such as stearic acid can be brominated by the method of Hell and Volhard to yield the 2-bromo-aliphatic acids which, on heating with alcoholic potassium hydroxide, yield the corresponding Δ^{2}-mono-ethylenic acids. These are compounds of higher melting point than isomeric acids in which the double bond is further removed from the carboxyl group (e.g. Δ^{2}-octadecenoic acid, m.p. 59°).[102]

By treating Δ^{2}-oleic acid with hydriodic acid and then heating the resulting iodostearic acid with alcoholic potash Eckert and Halla [103] produced the corresponding Δ^{3}-oleic acid, m.p. 56–57° ; this procedure has been repeated and further isomeric oleic acids have been synthesised.

Δ^{17}-octadecenoic acid and Δ^{16}-octadecenoic acid have been synthesised by condensation respectively of Δ^{10}-undecenoyl or Δ^{9}-undecenoyl chloride with the condensation product of ethyl 6-bromohexoate with acetoacetic ester (diethyl 2-acetylsuberate), leading to the respective 8-keto-octadecenoic acids which were reduced to the octadecenoic acids by hydrazine and sodium ethoxide.[265]

(v) **Synthetic homologues of oleic acid.** Reference may be made here to some synthetical preparations of acids related to the oleic series.

Methyl oleate and magnesium methyl iodide yield 2,2-dimethyl-Δ^{9}-octadecenol, which by further treatment is converted into the methyl ester of Δ^{8}-*heptadecenoic acid* ; this ester, by the same sequence of changes, gives Δ^{7}-*hexadecenoic acid.*[260]

The *cis-trans*-equilibrium mixture of the Δ^{15}-tetracosenoic acids was synthesised from erucyl (Δ^{13}-docosenyl) bromide by condensing the latter with malonic ester, followed by decarboxylation.[171] Similar syntheses of eicosenoic acid from octadecenyl iodide, etc., do not appear yet to have been effected.

OTHER ACYCLIC MONO-ETHENOID ACIDS

n-*Decenoic,* n-*Dodecenoic,* n-*Tetradecenoic Acids* ($C_{10}H_{18}O_2$, $C_{12}H_{22}O_2$, $C_{14}H_{26}O_2$)

Δ^9-Decenoic acid, $CH_2:CH.[CH_2]_7.COOH$, is the unsaturated acid of lowest molecular weight yet observed in any natural fat, and has so far only been detected in milk fat, especially cow milk fat (in which it only forms about 0·2 per cent. of the total acids). It is exceptional, as a natural unsaturated fatty acid, in possessing a terminal methylene group (ω-unsaturation); the double bond, however, occupies the same position, relative to the carboxyl group, as in oleic acid. The probable existence of this acid in butter fat was pointed out by Smedley[104] in 1912; it was first isolated, and its constitution determined by Grün and Wirth[105] in 1922, whilst in 1933 Bosworth and Brown[106] confirmed its structure and indicated the proportions in which it is present in cow milk fat.

Similar small amounts of **Δ^9-dodecenoic acid,** $CH_3.CH_2.CH:CH.[CH_2]_7.COOH$, were found in butter fat by Hilditch and Longenecker,[107] who confirmed the observations of Grün and Winkler,[108] and of Bosworth and Brown,[106] that this fat also contains over 1 per cent. of *Δ^9-tetradecenoic acid.*

A group of unsaturated C_{10}, C_{12}, and C_{14} acids of the general formula $CH_3.[CH_2]_m.CH:CH.[CH_2]_2.COOH$ ($m=4$, 6, or 8) has been observed to occur in small quantities in seed fats of certain sub-tropical plants belonging to the Lauraceæ (in which lauric acid is the main component). Toyama,[111] and Komori and Ueno,[111] showed in 1937 that all three acids—Δ^4-decenoic ("obtusilic"), Δ^4-dodecenoic ("linderic"), and Δ^4-tetradecenoic ("tsuzuic")—are present in the seed fat of *Lindera obtusiloba.* In 1927 Tsujimoto[112a] had noted the presence of small proportions of a do- and a tetra-decenoic acid in the seed fat of *L. hypoglauca,* but did not determine the position of the ethenoid bonds; in 1928, however, he[112a] obtained "tsuzuic" acid from the seeds of *Litsea glauca* and proved its constitution as Δ^4-tetradecenoic acid.

Δ^9-Tetradecenoic (myristoleic) acid, $CH_3.[CH_2]_3.CH:CH.[CH_2]_7.COOH$, accompanies Δ^9-hexadecenoic acid (below) in most marine animal liver and body (depot) fats, in which however it frequently amounts to not more than 1 per cent. and rarely to more than 4 or 5 per cent. of the total fatty acids. It is also found in very small proportions (usually below 0·5 per cent.) in the depot fats of the ox[109] and pig[110] and other land animals, in similar or sometimes slightly larger amounts in their liver glycerides and phosphatides and, as stated above, in cow and other milk fats. The tetradecenoic acid of all animal depot or liver fats yet studied has the above structure.

Although Δ^9-tetradecenoic acid has not been detected (in contrast to traces of Δ^9-hexadecenoic acid) as a normal trace component of seed fats, it has been observed in one instance, at present unique, to be a major component of a seed fat from the family Myristicaceæ. Atherton and Meara[113] found that the seed fat of *Pycnanthus Kombo* contained nearly 30 per cent. of this acid, in addition to 62 per cent. of myristic acid, in its component fatty acids.

Just as certain *Lindera* species produce a Δ^4-tetradecenoic acid in their seed fats, so, in the animal kingdom, the head oil of the sperm whale contains a third isomeric form of this acid. Hilditch and Lovern[20] found that sperm head oil contained about 14 per cent. of a tetradecenoic acid, in addition to about 4 per cent. of a dodecenoic acid; the first-mentioned acid had previously been found by Tsujimoto[112b] to be Δ^5-tetradecenoic acid, thus differing from the Δ^9-tetradecenoic acid of marine animal depot and liver fats.

Δ^9-Hexadecenoic (palmitoleic, zoomaric) acid, $CH_3.[CH_2]_5.CH{:}CH.[CH_2]_7.COOH$, is now known to be a constituent of nearly all natural fats, but it is a very subordinate component except in marine animal oil glycerides and in the glycerides and phosphatides of the livers of land animals. The acid was first noticed as early as 1854 by Hofstädter[114] among the mixed acids of the head oil of the sperm whale, and was in consequence named physetoleic acid. In 1898 Ljubarsky[115] isolated it from seal oil, and in 1906 Bull[116] obtained it in a comparatively pure condition from the mixed acids of cod liver oil, and confirmed its molecular composition as $C_{16}H_{30}O_2$. The name palmitoleic acid, in view of its content of sixteen carbon atoms in the molecule, was proposed by Lewkowitsch in 1906. From about 1924 onwards the acid was observed as a regular component of many marine animal oils, in which it usually forms about 15–20 per cent. of the total fatty acids present. Its structure was established in 1925 as that of Δ^9-hexadecenoic acid by Armstrong and Hilditch,[117b] who showed that its methyl ester, when oxidised in solution in acetone by powdered potassium permanganate, gave good yields of *n*-heptanoic and azelaic acids. In 1924 Toyama[118] stated that an acid of the formula $C_{16}H_{30}O_2$ was present in the blubber of the humpbacked whale, *Megaptera longimana* Rudolphi, to which he gave the name zoomaric acid. Toyama isolated the same acid from a number of other marine animal oils (including some oils from Elasmobranch fish, such as rays and sharks[119]) and, in 1927, showed[120] that the products of disruptive oxidation of zoomaric acid from the oils of the humpback whale, sei-whale (*Balænoptera borealis* Less.), and other whales, and from cod liver oil, were in all cases *n*-heptanoic and azelaic acids, so that zoomaric and palmitoleic acids are synonymous. Other investigators have shown that the palmitoleic acid present in the head and blubber oils of the sperm whale,[20, 121] seal oil,[122], Scottish cod liver oil,[123] and porpoise blubber[124] is also Δ^9-hexadecenoic acid. In the meantime it had been demonstrated that palmitoleic acid, isolated respectively from seal oil,[125] cod liver oil,[123] humpbacked whale oil,[118] and South Antarctic whale oil,[117b] yielded palmitic acid on hydrogenation, and thus belonged to the normal series of higher aliphatic acids.

Since the hexadecenoic acid present in all marine animal oils so far examined has the same constitution, it seems desirable to refer to it by its systematic name (Δ^9-hexadecenoic acid) and to allow the older and empirical terms " palmitoleic " or " zoomaric " acid to lapse. The adjective " palmitoleic " might be thought to convey a suggestion that the acid is biochemically related to either palmitic or oleic acid, but there is in fact no evidence yet available to determine whether this may be the case or not. Equally, " zoomaric " has now no precise significance, for Δ^9-hexadecenoic acid is by no means the only characteristic acid of the fats of marine animals, whilst it has now been demonstrated that it occurs, in small or in large proportions, in all classes of fats, vegetable and animal.

Δ^9-Hexadecenoic acid is, it is true, most abundant in fats of aquatic origin, but is not confined to those of aquatic fauna. Lovern[126] has shown that the fats of fresh-water and marine algæ and diatoms contain over 30 per cent. of unsaturated C_{16} acids, in which polyethenoid C_{16} acids are also present in addition to hexadecenoic acid, and that the proportion of the latter in fresh-water fish and zooplankfon is greater than in those of marine species.

The depot fats so far examined of amphibia [127, 128, 129] and reptiles [128, 130] contain nearly as much hexadecenoic acid (8–15 per cent.) as the majority of fish fats, whilst depot fats of rats [131] and birds [132] contain somewhat less (6–8 per cent.). Similar proportions of Δ^9-hexadecenoic acid are present in the liver glycerides [133] of the larger mammals (ox, sheep, pig), but in the corresponding depot fats [109, 134] the amount is smaller (2–3 per cent.). The milk fats of the cow [107, 135] and the goat [136] have also been shown to contain about 3–4 per cent. of Δ^9-hexadecenoic acid.

Hexadecenoic acid is also, probably, a regular component of all phosphatides. In the liver phosphatides of the ox, sheep, and pig it is less abundant than in the corresponding liver glycerides, and forms only about 5 per cent. of the total phosphatide fatty acids.[133] It may also form up to 5 per cent. or so of the fatty acids present in many vegetable seed phosphatides.[137]

Amongst the lower forms of land flora, hexadecenoic acid has been observed in quantity in the fats of diphtheria bacilli,[138] of yeast [139] and of the spores of a cryptogam (*Lycopodium*).[140] In the storage fats of the more developed land plants it has recently been proved that the following oils contain up to, but rarely more than, 1 per cent. of hexadecenoic acid: groundnut,[141] olive,[142] teaseed,[142] cottonseed,[143] soya bean,[143] and palm oils.[143] In the case of the acid from soya bean oil, its constitution was determined to be Δ^9-hexadecenoic acid.[144]

Δ^9-Hexadecenoic acid (no other structural isomeride has yet been discovered in nature) has thus been found in fats from all kinds of living organisms; but the most interesting feature of its occurrence is the circumstance that it is a major component acid in fats from the lower forms of life and in those of the more developed forms of aquatic flora and fauna, whilst it is only present in very small amounts in the depot fats of land flora and fauna at the other end of the evolutionary scale. Moreover, in the fats of animals, a progressive diminution occurs in the proportion of hexadecenoic acid corresponding with the evolutionary development of the species. Hexadecenoic acid thus takes a place with oleic, palmitic, and perhaps stearic acids as one of the few fatty acids which appear to be common to all fats.

On isomerisation with oxides of nitrogen or selenium Δ^9-hexadecenoic acid is partly transformed into a solid elaidic or *trans-* form of the acid. Oxidation of the natural *cis-* acid with peracetic acid leads to a 9, 10-dihydroxypalmitic acid, m.p. 87°, whilst its oxidation with dilute highly alkaline aqueous permanganate solution at 0° furnishes an isomeric 9, 10-dihydroxypalmitic acid of higher melting-point, 125°.

Hydroxyhexadecenoic acids and trihydroxypalmitic acids.—These, although not constituents of natural fats, may be mentioned here owing to their occurrence in two other natural products of entirely different nature.

Ambrettolide, the component of vegetable musk oils which confers upon them their distinctive odour, is an internal anhydride or lactone of 16-hydroxy-Δ^7-hexadecenoic acid.[261a] It has apparently not yet been produced synthetically, but isomeric forms, some of which possess the musk odour, have been synthesised by Collaud (*iso*-ambrettolide, lactone of 16-hydroxy-Δ^6-hexadecenoic acid [261b]) and by Mitter and Bhattacharya (*epi*-ambrettolide, lactone of 16-hydroxy-Δ^9-hexadecenoic acid [262c]).

Aleuritic acid, 9, 10, 16-*trihydroxypalmitic acid*, is an integral part of shellac, in which it is united with shellolic acid and perhaps other constituents to form the lac resin. Its constitution has been determined by Nagel *et al.*[262a] Mitter and Mukherjee [262b] synthesised 16-methoxy-Δ^9-hexadecenoic acid from 6-methoxy-*n*-hexyl bromide and 7-chloroheptaenal by the procedure of Noller and Bannerot,[78] from which 16-methoxy-9,10-dihydroxypalmitic acid and eventually aleuritic acid should be produced.

Reduction of ethyl aleuritate with sodium in butyl alcohol gives aleurityl alcohol (1,9,10,16-tetrahydroxyhexadecane).[262b] With phosphorus tetraiodide in ether, aleuritic acid furnished 16-iodo-Δ^9-hexadecenoic acid, the silver salt of which yields the lactone of 16-hydroxy-Δ^9-hexadecenoic acid (an isomer of ambrettolide, *cf.* above).[262c]

The conversion of aleuritic acid into the equilibrium mixture of *cis*- and *trans*-Δ^9-hexadecenoic acids (and thence, by alkaline permanganate oxidation of the latter, into the isomeric 9, 10-dihydroxypalmitic acids, m.p., respectively, 125° and 89–90°) has been effected by Nagel and Mertens.[262d]

Octadecenoic acids

A number of structural isomerides of oleic acid have been reported as constituents of natural fats from time to time. Most of these have turned out to be cases of mistaken identity, and only two have survived the scrutiny of modern investigation, namely, petroselinic acid, characteristic of Umbelliferous seed fats, and vaccenic acid, which occurs in very small proportions in the milk and depot fats of the cow and possibly other herbivorous animals.

Δ^6-Octadecenoic (petroselinic) acid, $CH_3.[CH_2]_{10}.CH{:}CH.[CH_2]_4.COOH$. This acid, which accompanies ordinary oleic and linoleic acids as a major component in seed fats of the families Umbelliferæ and Araliaceæ, was first noted in 1909 in parsley seed oil by Vongerichten and Köhler,[145] who established its structure by Baruch's method and described its chief properties. In the same year Scherer [146] observed the acid in the seed fats of two other Umbellates (*Pimpinella anisum* and *Fœniculum capillaceum*), and in 1914 Palazzo and Tamburelli [147] showed that it was present in ivy seed oil (Araliaceæ). Later work by Hilditch with Miss Jones [148] and Christian [149] on the seed fats of a large number of other Umbelliferous species showed that it was present in all cases in amounts varying from 20 to 75 per cent. of the mixed fatty acids. The constitution of the acid from parsley seed oil has been confirmed by ozonolysis or permanganate-acetone oxidation by Eibner, Widenmayer and Schild,[150] by Hilditch and Miss Jones,[151] and by van Loon,[152] whilst the amount (55 per cent.) of petroselinic acid in ivy seed oil was determined by Steger and van Loon.[153]

Petroselinic acid melts at 30° and its lead salt, in common with those of other oleic acids which are solid at the ordinary temperature, is sparingly soluble in cold alcohol and ether. The acid is transformed, by contact with oxides of nitrogen, into an equilibrium mixture of the geometrical isomerides containing about 60 per cent. of *trans*-Δ^6-octadecenoic acid, which melts at 53°. Oxidation with Caro's acid [154] or peracetic acid [151] yields a 6,7-dihydroxystearic acid, m.p. 114–115°, whilst oxidation by dilute alkaline permanganate [151, 154] produces an isomeric acid, m.p. 122°.

Δ^{11}-Octadecenoic (vaccenic) acid, $CH_3.[CH_2]_5.CH{:}CH.[CH_2]_9.COOH$, was observed by Bertram,[155] who stated that it occurred to the extent of 1 per cent. in beef fat and 0·01 per cent. in butter fats, melted at 39°, and gave on oxidation *n*-heptanoic acid and a dicarboxylic acid $COOH.[CH_2]_9.COOH$.

Grossfeld and Simmer[156] reported the presence of vaccenic acid in the following fats: butter (1–4·7 per cent.), beef fat (1·6 per cent.), mutton fat (1–2 per cent.), lard (0·2 per cent.). Boeseken *et al.*[157] found that vaccenic esters are present in some quantity amongst the products of partial hydrogenation of elæostearic esters.

It may be added that there is some reason to believe that the monoethenoid acids of whale and fish oils may include, in addition to much oleic acid, minor proportions of a structural isomeride or isomerides, the constitution of which has however not been settled.[117a] The presence of Δ^{11}- as well as Δ^{9}-octadecenoic acid in menhaden oil has been reported.[158]

The individuality or otherwise of the oleic acid in a number of fats has been scrutinised by Millican and Brown[281] by careful study of the acids isolated and purified by a combination of fractional distillation and low-temperature crystallisation of the methyl esters. In vegetable fats, these workers find that the octadecenoic acids of olive, cottonseed, maize and linseed oils are wholly oleic acid, but that those of soya bean and or rapeseed oil appear to be mixtures predominating in Δ^{9}-octadecenoic (oleic) acid, but with some other isomeric octadecenoic acid also present. Similarly, they found evidence of other isomeric acids in addition to oleic (the principal component) in the octadecenoic acids of lard, beef tallow, adrenal phosphatides, pig liver lipids, and human depot fat, and consider that in these animal fats the isomer is probably the vaccenic acid described by Bertram (*cf.* above).

Eicosenoic acids, $C_{20}H_{38}O_2$.

Δ^{9}-**Eicosenoic (gadoleic) acid,** $CH_3.[CH_2]_9.CH{:}CH.[CH_2]_7.COOH$, was first noticed by Bull[116] in cod liver oil in 1906. It has since been found widely distributed in fish and marine mammalian oils, although not so abundantly as hexadecenoic acid (it probably rarely amounts to more than 5–10 per cent. of the total fatty acids). Takano[159] showed in 1933 that gadoleic acid from sardine oil possessed the Δ^{9} structure, and Toyama and Tsuchiya[160] subsequently found the same structure in the acid from cod liver, herring, and whale oils; the latter workers observed an isomeric (" gondoic ") acid in the blubber fat of the pilot whale.

Δ^{11}-**Eicosenoic acid,** $CH_3.[CH_2]_7.CH{:}CH.[CH_2]_9.COOH$, has only been observed[161] in the vegetable kingdom—in the unusual liquid seed wax of *Simmondsia californica* (*cf.* Chapter IV, p. 185). Here it is the chief component acid and, with minor amounts of erucic acid, is combined with a mixture of Δ^{11}-eicosenyl and Δ^{13}-docosenyl alcohols (*cf.* Chapter X, p. 457).

Baldwin and Parks,[158] however, state that this isomer of gadoleic acid is present in menhaden oil.

Docosenoic acids, $C_{22}H_{42}O_2$.

Δ^{11}-**Docosenoic (cetoleic) acid,** $CH_3.[CH_2]_9.CH{:}CH.[CH_2]_9.COOH$, accompanies gadoleic acid (usually in smaller proportions than the latter) in many marine animal oils. Formerly believed to be identical with the erucic acid of vegetable fats, it was shown by Toyama[162] to have the Δ^{11} structure.

Δ^{13}-**Docosenoic (erucic) acid,** $CH_3.[CH_2]_7.CH{:}CH.[CH_2]_{11}.COOH$, is an important vegetable fatty acid which, so far as is known at present, is confined to seed fats of the natural families Cruciferæ and Tropæolaceæ; in these, however, it appears to be widely distributed. It forms from 40 to 50 per cent. of the mixed fatty acids of rape, mustard seed, wallflower seed, and other Cruciferous oils, from which it may be isolated, according to Holde and Wilke,[163] by precipitating as the sparingly soluble lead salt, followed by subsequent repeated crystallisation of the regenerated acids from alcohol in order to separate accompanying saturated acids. Täufel and Bauschinger[164] recommend treating mixed rape oil fatty acids with sufficient lead acetate to combine with about 4 per cent. of the total fatty acids, and then to obtain the erucic acid from the uncombined part of the original acids by fractional precipitation as magnesium salt. Probably a better method than either of these is to precipitate most of the saturated acids as recommended by Täufel and Bauschinger, and then to convert the remaining acids into methyl esters and separate the erucic acid ester from the mixture of erucic, oleic, and linoleic esters by fractional distillation; finally the erucic acid obtained may be further purified by recrystallisation from alcohol.

A better source of erucic acid (at all events for laboratory purposes) than Cruciferous oils is nasturtium seeds.[165] Although the latter only contain about 8 per cent. of fat, erucic acid forms 80 per cent. of the fatty acids of the latter, and may readily be obtained therefrom by fractional distillation of the methyl esters of the mixed acids, or even by simple crystallisation of the latter from 70 per cent. alcohol. This seed fat contains nearly 40 per cent. of trierucin, which, again, may be isolated from it by direct crystallisation.

The pure acid melts at 33·5° and has an iodine value of 74·7. Like other higher mono-ethylenic acids which are solid at the ordinary temperature, erucic acid yields a lead salt which is sparingly soluble in ether and alcohol. On isomerisation with oxides of nitrogen it yields *trans*-Δ^{13}-docosenoic acid, brassidic acid, which melts at 60°. Oxidation of erucic acid by peracetic acid or by Caro's acid yields a 13,14-dihydroxybehenic acid, m.p. 99–100°, whilst alkaline permanganate oxidation produces an isomeric acid, m.p. 130–131°.[82, 166] Green and Hilditch[91] showed that, on further oxidation with aqueous alkaline permanganate, the 13,14-dihydroxybehenic acids (like the 9,10-dihydroxystearic acids, p. 407) undergo scission into oxalic acid, *n*-octanoic acid and sebacic acid ($COOH.[CH_2]_{10}.COOH$), but that they are attacked with much greater difficulty than the 9,10-dihydroxystearic acids. Kaufmann and Fiedler[167] state that this difference in ease of oxidation can be employed as a means of determining erucic acid in a mixture of the latter with oleic and linoleic acids: the mixed acids are oxidised with aqueous alkaline permanganate solution under prescribed conditions which permit the erucic acid to be determined as dihydroxybehenic acid, the oleic and linoleic acids having been completely converted into water-soluble mono- and di-carboxylic acids.

The constitutional formula of erucic acid follows from the facts that on catalytic hydrogenation it passes completely into behenic acid and that on oxidation it yields a mixture of *n*-nonanoic acid and brassylic acid, $COOH.[CH_2]_{11}.COOH$.[168]

Tetracosenoic acid, $C_{24}H_{46}O_2$.

Δ^{15}-**Tetracosenoic (selacholeic, nervonic) acid**, $CH_3.[CH_2]_7.CH:CH.[CH_2]_{13}.COOH$, seems to be a characteristic component of the fats of many Elasmobranch fish, but it has not been noticed in Teleostid fish or in marine mammalia; it was first reported in 1927 by Tsujimoto[169] (selacholeic acid), who determined its constitution. In the same year Klenk[170a] isolated the same acid (which he termed nervonic acid) from the cerebrosides of brain tissue, and also established its structure. In 1930 Hale, Lycan, and

Adams[171] synthesised the Δ^{15}-tetracosenoic acids by condensing erucyl (Δ^{13}-docosenyl) bromide, $CH_3.[CH_2]_7.CH{:}CH.[CH_2].{}_{11}CH_2Br$, with malonic ester. Hydrolysis of the product gave a mixture of acids of the structure $CH_3.[CH_2]_7.CH{:}CH.[CH_2]_{13}.COOH$; one, melting at 39°, was identical with the natural selacholeic and nervonic acids, and the other, m.p. 61°, was the *trans-* form corresponding to the *cis-* acid of m.p. 39°.

Hexacosenoic and Tricosenoic acids, $C_{26}H_{50}O_2$ and $C_{30}H_{58}O_2$, occur in the seed fat of the Indian shrub *Ximenia americana* (Olacaceæ) ; according to Boekenoogen,[172] the mixed fatty acids contain about 25 per cent. of Δ^{17}-hexacosenoic (" ximenic ") acid and about 5 per cent. of Δ^{21}-tricosenoic (" lumequic ") acid.

Klenk and Schumann[170b] stated that a hexacosenoic acid, m.p. 45°, accompanies nervonic acid (*cf.* above) in brain cerebrosides.

HYDROXY-MONO-ETHENOID ACID

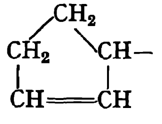
12-Hydroxy-Δ^9-octadecenoic (Ricinoleic) acid, $CH_3.[CH_2]_5.CH(OH).CH_2.CH{:}CH.[CH_2]_7.COOH$, forms over 80 per cent. of the mixed acids of castor seed oil (*Ricinus communis*), in which it was apparently discovered by Saalmüller.[173] It has also been reported from time to time as a very minor component of certain other oils, but it is doubtful whether it occurs very frequently in quantity in nature apart from *Ricinus* species. Gurgel and de Amorim[174] have stated that ricinoleic acid forms about 47 per cent. of the mixed fatty acids of ivory wood oil, the seed fat of *Agonandra brasiliensis* ; according to Margaillan,[175] the oil of *Wrightia annamensis* also contains as its chief component a hydroxyoleic acid probably identical with ricinoleic acid.

Ricinoleic acid melts at 5° and is optically active ($[\alpha]_D+6{\cdot}7$). The lead salt of the acid is soluble in ether but very sparingly soluble in light petroleum. When the acid is treated with oxides of nitrogen it is partially transformed into the *trans-* isomeride, ricinelaidic acid, m.p. 52–53°, $[\alpha]_D+6{\cdot}7$. Oxidation of ricinoleic acid by alkaline permanganate yields two 9,10,12-trihydroxystearic acids, m.p. 110–111° and 140–142°.[176] More energetic oxidation of ricinoleic acid with potassium permanganate leads to the production of azelaic acid (Maquenne,[177] 1899), which indicates that the double bond is in the Δ^9 position. Destructive distillation of the acid, or better of its sodium or calcium salt, produces a mixture of œnanthaldehyde and Δ^{10}-undecenoic acid * (Goldsobel,[178a] 1894 ; Vernon and Ross,[178a] 1936) ; dry distillation of potassium ricinoleate with excess of potassium hydroxide liberates methyl-*n*-hexylcarbinol and leaves the potassium salt of sebacic acid (Freund and Schönfeld,[178b] 1891). By Baruch's sequence[54] of reactions (*cf.* p. 399), Goldsobel[178a] showed that ricinoleic acid is 12-hydroxy-Δ^9-octadecenoic acid.

A lævorotatory isomer of ricinoleic acid, $[\alpha]_D-8°$, is stated by Vidyarthi and Mallya[263] to form 60 per cent. of the component acids of the seed fat of *Vernonia anthelmintica* (Compositæ) ; the hydroxyl group may occupy a different position to that in ricinoleic acid.

CYCLIC MONO- (AND DI-) ETHENOID ACIDS

A small group of acids, characterised chemically by the presence of a cyclopentenyl ring-system



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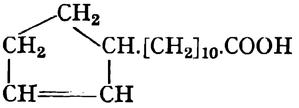
* Δ^{10}-Undecenoic acid was formally synthesised for the first time by Gaubert, Linstead, and Rydon[179] in 1938.

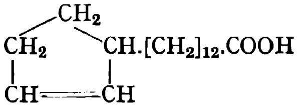
in the fatty acid chain, is found in quantity in the seed fats of *Hydnocarpus* and a few other genera of the tropical family Flacourtiaceæ (Chapter IV, p. 181). These fats are also specific in their therapeutic value in the treatment of leprosy and some other diseases. The acids in question are hydnocarpic ($C_{16}H_{28}O_2$), chaulmoogric ($C_{18}H_{32}O_2$), and gorlic ($C_{18}H_{30}O_2$); they are all optically active (dextrorotatory). Chaulmoogric acid is probably the most abundant of the three, but hydnocarpic acid is also an important component of these seed fats in some cases; these two acids are mono-ethenoid. Gorlic acid is di-ethenoid, and accompanies chaulmoogric acid in lesser proportions in some of the Flacourtiaceæ seed fats. The structural formulæ of the acids are as follows:

$C_{16}H_{28}O_2$
Hydnocarpic
11-Δ^2-Cyclopentenyl-*n*-undecanoic



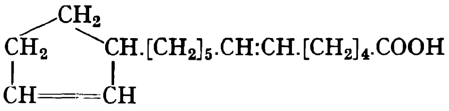
M.p. 59–60°
$[\alpha]_D+68^\circ$

$C_{18}H_{32}O_2$
Chaulmoogric
13-Δ^2-Cyclopentenyl-*n*-tridecanoic



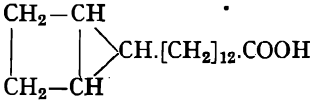
M.p. 71°
$[\alpha]_D+56^\circ$

$C_{18}H_{30}O_2$
Gorlic
13-Δ^2-Cyclopentenyl-Δ^6-tridecenoic



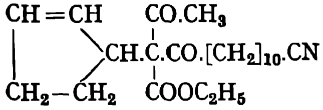
liquid
$[\alpha]_D+60^\circ$

The chemical constitution of chaulmoogric acid (and of the nearly related hydnocarpic acid) was first studied exhaustively in 1904–1907 by Power and Barrowcliff[180] who showed by systematic investigation of the products of oxidation with permanganate and other reagents that, amongst other acids the following products were obtained in the case of chaulmoogric acid: 1,14-tetradecane-di-acid, $COOH.[CH_2]_{12}.COOH$; 1,4,17-heptadecane-tri-acid, $COOH.[CH_2]_2.CH(COOH).[CH_2]_{12}.COOH$; 4-keto-1,17-heptadecane-di-acid; $COOH.[CH_2]_2.CO.[CH_2]_{12}.COOH$. From these reactions Power and Barrowcliff concluded that the structure of chaulmoogric acid was best represented as a tautomeric mixture of the cyclopentene derivative shown in the above formula with the cyclopropane compound:

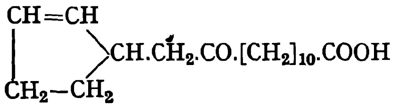


Later Shriner and Adams,[181] as a result of further study of the reactions and decomposition products of chaulmoogric acid, showed that it was satisfactorily represented by the cyclopentenoid fotmula alone, and in 1927

Perkins and Cruz [182] succeeded in synthesising racemic chaulmoogric acid by condensing 11-cyano-undecanoic acid, $CN.[CH_2]_{10}.COOH$, with acetoacetic ester and subsequently condensing the reaction product with sodium and Δ^2-chlorocyclopentene when the compound



was obtained; on hydrolysis this gave a yield of about 30 per cent. of the keto-acid



which, by reduction with hydrazine and sodium ethylate under pressure, was converted into *dl*-chaulmoogric acid.

Hydrogenation of chaulmoogric acid yields the optically inactive dihydrochaulmoogric (13-Δ^2-cyclopentyl-*n*-tridecanoic) acid,[183] m.p. 71–71·5°.

A synthesis of *dl*-hydnocarpic acid has been effected by Bokil and Nargund.[264a]

Lower analogues of chaulmoogric and hydnocarpic acids have been isolated in small quantities from some of the *Hydnocarpus* seed fats by Cole and Cardoso,[186a] including:

ACID	FORMULA	CONSTITUTION	M.p.
Aleprolic	$C_6H_8O_2$	Δ^2-Cyclopentenyl carboxylic	liq.
Aleprestic	$C_{10}H_{16}O_2$	5-Δ^2-Cyclopentenyl-*n*-pentanoic	liq.
Aleprylic	$C_{12}H_{20}O_2$	7-Δ^2-Cyclopentenyl-*n*-heptanoic	32°
Alepric	$C_{14}H_{24}O_2$	9-Δ^2-Cyclopentenyl-*n*-nonanoic	48°

3-Cyclopentenylpropionic acid and 11-cyclohexylundecanoic acid have been prepared synthetically by Bokil *et al.*[264b]

Buu-Hoi [286] has shown that acids of the chaulmoogric series may be degraded to members of successively lower carbon content by the following sequence of actions:

$$R.CH_2.COOEt \xrightarrow{C_6H_5.MgBr} R.CH_2.C(OH).(C_6H_5)_2$$

$$\rightarrow R.CH{=}C(C_6H_5)_2 \xrightarrow{CrO_3} R.COOH + (C_6H_5)_2CO.$$

In this way he has converted chaulmoogric acid in two stages into hydnocarpic acid, and the latter similarly into alepric acid.

The di-ethenoid gorlic acid contains an additional double linking in the aliphatic chain. It was first detected by Wrenshall and Dean [184] in 1924, whilst in 1928 André and Jouatte [185] showed that it formed about 10 per cent. of the acids of gorli seed oil. Its structure as a Δ^6-tridecenoic acid was proved in 1938 by Cole and Cardoso.[186b]

ACETYLENIC ACIDS

Although several acetylenic (ethynoid) acids have been artificially prepared from the corresponding natural acids of the oleic series (notably

Δ^{9}-octadecynoic or stearolic acid from oleic acid), their occurrence in nature is very rare and confined to one or two instances.

$CH_3\cdot(CH_2)_{10}\cdot C\equiv C\cdot(CH_2)_4\cdot COOH$

Δ^{6}-**Octadecynoic (Tariric) acid,** $CH_3.[CH_2]_7.C \vdots C.[CH_2]_7.COOH$, is the only well-defined example of a natural acetylenic acid, and this has only been observed in seed fats of the Central American genus *Picramnia* (Simarubaceæ). Arnaud,[187] in 1892, first reported it in the seed fat of *P. Sow* (tariri fat); he obtained lauric and adipic acids from it as the result of oxidation, and ascribed the above structure to the acid. In 1910 Grimme[188] stated that the acid was present in the seeds of *P. Carpenteræ*, and, in 1912, that it formed about 20 per cent. of the component acids of the seed fat of *P. Linderiana*. In 1933 Steger and van Loon[189] showed that the fat from *P. Sow* contained over 90 per cent. of glycerides of tariric acid, the only other components being saturated acids; they also confirmed the constitution of the acid (by oxidation with ozone).

A peculiar **octadecen-diynoic acid** was observed by Steger and van Loon[190a] (1937) to be a major component of the seed fatty acids of *Onguekoa Gore* (Olacaceæ). It was later shown by Boekenoogen[190b] and by Castille[190c] to possess a terminal ethenoid group and to yield oxalic and adipic acids, with ethyl hydrogen azelate, on oxidative scission, so that its structure must be represented by one of the formulæ:

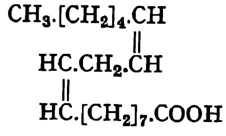
$$CH_2{=}CH.C \vdots C.[CH_2]_4.C \vdots C.[CH_2]_7.COOH$$

$$CH_2{=}CH.[CH_2]_4.C \vdots C.C \vdots C.[CH_2]_7.COOH.$$

Doucet and Fauve[190d] favour the second formula (with conjugated ethynoid bonds). It melts at 39·5° and was termed "isanic" acid by Steger and van Loon, and "erythrogenic" acid by Castille.

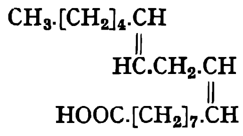
POLYETHENOID ACIDS WITH TWO DOUBLE BONDS

These have only been definitely recognised so far in the case of the acids of the C_{18} series; and here, until recently, it was considered that the only representative was *linoleic acid*, one of the four possible geometrical forms of $\Delta^{9,12}$-octadecadienoic acid (probably the *cis* Δ^{9}-, *cis* Δ^{12}-isomeride):



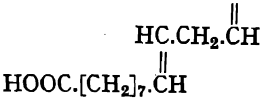
$$\begin{array}{l} CH_3.[CH_2]_4.CH \\ \qquad\qquad\quad \| \\ HC.CH_2.CH \\ \;\| \\ HC.[CH_2]_7.COOH \end{array}$$

9 *cis*–12 *cis*



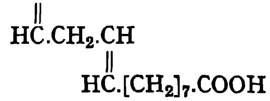
$$\begin{array}{r} CH_3.[CH_2]_4.CH \qquad\; \\ \| \qquad\qquad \\ HC.CH_2.CH \\ \| \\ HOOC.[CH_2]_7.CH \end{array}$$

9 *cis*–12 *trans*



$$\begin{array}{r} CH_3.[CH_2]_4.CH \\ \| \\ HC.CH_2.CH \\ \| \qquad\quad \\ HOOC.[CH_2]_7.CH \qquad\quad \end{array}$$

9 *trans*–12 *cis*



$$\begin{array}{l} CH_3.[CH_2]_4.CH \\ \qquad\qquad\quad \| \\ \qquad\qquad HC.CH_2.CH \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad HC.[CH_2]_7.COOH \end{array}$$

9 *trans*–12 *trans*

Recent work has, however, made very doubtful the existence of more than minor quantities of octadecadienoic acids in fats of aquatic origin, and has also failed to show the presence of the typical linoleic acid of the land vegetable kingdom amongst any octadecadienoic acids present. It has become equally clear that the characteristic octadecadienoic acid, which usually accompanies oleic acid in minor amounts in land animal fats, is not " linoleic acid," although it is most probably another form of the $\Delta^{9,12}$-octadecadienoic acids. It is generally considered at present that the small amounts of " vegetable linoleic " acid which in some cases are also present in the fats of higher land animals have most probably been assimilated from ingested vegetable sources, and not produced by the animal.

cis-cis-$\Delta^{9,12}$-**Octadecadienoic or linoleic acid** is practically as widely distributed in the vegetable kingdom as ordinary oleic acid ; it appears to have first been recognised as an individual acid by Sacc [191] in 1844. In many vegetable fats its amount is subordinate to that of oleic acid, but, of course, in the " semi-drying " and " drying " classes of seed oils it is a major component of the mixed fatty acids. Linoleic acid is liquid at ordinary temperatures and forms a lead salt comparatively freely soluble in ether and alcohol, and a lithium salt soluble in alcohol and, to a less extent, in acetone. Its isolation in the pure condition is therefore not easy by any simple physical method ; but Brown and co-workers [192a] have shown that by crystallisation from solvents at very low temperatures it is possible to separate linoleic from oleic acid and to obtain a high degree of purity in the linoleic acid finally isolated.

The following directions for isolating seed-fat linoleic acid in 98–100 per cent. purity by low-temperature fractional crystallisation of the fatty acids of maize, cottonseed, grapeseed, sesame or poppyseed oils have been given by Brown *et al.*,[192a] (1941, 1943). The mixed fatty acids of the oil, dissolved in acetone (75 g. per litre) are cooled with stirring first at −20° and then at −50°, and the separated crystals removed ; the solvent is further cooled to −70°, when a concentrate containing about 90 per cent. linoleic acid separates. This is recrystallised from light petroleum, b.p. 30–60° (65 g. per litre) at −48°, when crystals containing 95 per cent. linoleic acid separate, and are recrystallised from light petroleum (6·25 g. per litre) at −60° to −62°, to give nearly pure linoleic acid. The iodine values of the acids prepared from the five oils mentioned ranged from 178·4 to 180·8 (theory 181·4), and the melting points from −5·8° to −5·2°. The yields of pure acid obtained are apparently about 30–35 per cent. of the linoleic acid present in the oils.

From pure linoleic acid, Riemenschneider *et al*,[252b] have prepared trilinolein which, after being purified by molecular distillation, yielded dimorphic forms which melted at −43° and −13°. Daubert and Baldwin [278] give these melting points as −45·6° and −12·9°.

The only other—and hitherto usually adopted—method of obtaining a pure linoleic acid is to add bromine to the unsaturated acids of a seed fat, when nearly half of the linoleic acid is converted into a crystalline tetrabromostearic acid, m.p. 114°, which is insoluble in light petroleum. Debromination of this product with zinc yields a so-called " α "-linoleic acid * which, at the hands of several workers, has been shown by ozonisation or permanganate-acetone oxidation to be almost entirely $\Delta^{9,12}$-octadecadienoic acid.

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* It should be emphasised that the division of natural linoleic and linolenic acids, as frequently practised by investigators in this field, into " α "- and " β "-forms has no structural significance, and only means that the " α "-acid is that which has been isolated in the form of a crystalline, insoluble bromo-adduct, the so-called " β "-acid representing the remainder.

This " α "-linoleic acid, when re-brominated, again gives slightly less than half the theoretical yield of crystalline tetrabromostearic acid, the remainder being a liquid form (or forms) of tetrabromostearic acid freely soluble in light petroleum. Debromination of these soluble products furnishes the so-called " β "-linoleic acid,* which is probably a mixture of acids of, at present, somewhat uncertain composition, but in which other geometrical isomerides of $\Delta^{9,12}$-octadecadienoic acid are doubtless the main constituents (see below).

On oxidising either seed fat or regenerated " α "-linoleic acid with aqueous alkaline permanganate (Hazura [193]) a mixture of two tetrahydroxystearic (sativic) acids results, one of which melts at 171–173° and the other at 157–159°.†

The constitution of the linoleic acid in linseed,[195] cottonseed,[196], soya bean,[197] poppy seed,[197] and groundnut [198] oils has been determined by ozonisation or permanganate-acetone oxidation, whilst that from many other seed fats has been shown to yield the same " α "-tetrabromostearic acid m.p. 114°, and the two sativic acids just mentioned ; so that it is reasonably certain that linoleic acid from all these vegetable fats is the one form of $\Delta^{9,12}$-octadecadienoic acid.

The stereochemical configuration of other natural vegetable fat linoleic acids is less certain, although it is now more or less agreed that only one form occurs naturally, and that this is the *cis* Δ^{9}-*cis* Δ^{12}-acid.

The production of two tetrabromo- and two tetrahydroxy-stearic acids from linoleic acid led Bedford [199] in 1906 to conclude that two isomeric (" α "- and " β "-) linoleic acids were originally present, but in 1909 Rollett [200] showed that the " α "-linoleic acid regenerated from the crystalline tetrabromo-acid again yields a mixture of liquid and solid tetrabromostearic acids, and therefore concluded that a single natural isomer was concerned, which, on bromination, gave two tetrabromostearic acids each related to a different geometrical isomeride of the octadecadienoic acid. Nicolet and Cox [201] in 1922 showed that, by addition of hypochlorous acid and subsequent treatment with alkali, seed fat linoleic acid gives, not the above two " sativic " acids, but small yields of two other tetrahydroxystearic acids, m.p. 144° and 135°. By considering the various pairs of isomeric tetrahydroxystearic acids possible from the four geometrically isomeric forms of the octadecadienoic acid (p. 332), and with the further assumption that (as is known to be the case with the dibromostearic acids from oleic and elaidic acids) no change of configuration occurs during addition of bromine (or its subsequent removal) at the Δ^{9} position, Nicolet and Cox concluded that (taking oleic acid as the *cis*- form ‡) the natural linoleic acid must be a mixture of the following forms : *cis* Δ^{9}-*cis* Δ^{12}-, and *cis* Δ^{9}-*trans* Δ^{12}-octadecadienoic acid.

In 1931 Suzuki and co-workers [202] studied the partial debromination of di- and tetra-bromostearic acids, and (by oxidation) the constitution of the dibromo-octadecenoic acids so obtained from tetrabromostearic acid, and finally reached the conclusion that " α "-linoleic acid was the *cis* Δ^{9}-*cis* Δ^{12}-, and " β "-linoleic acid the *trans* Δ^{9}-*trans* Δ^{12}-isomer. (The details of the arguments, in both Nicolet and Cox's and Suzuki's work, are very intricate, and it is not practicable here to give them completely; the original papers should be consulted by those who require a complete statement of the case.)

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* See note on previous page.

† According to Birosel,[194] supported by Riemenschneider *et al.*,[204] the acid melting at 157–159° is a eutectic mixture of that melting at 173° with an acid of m.p. 163·5°.

‡ Nicolet and Cox naturally, at the time of their work, assumed oleic to be the *trans*-acid ; their argument is here expressed in terms of the present view that oleic is the *cis*-form of Δ^{9}-octadecenoic acid.

In 1935 Green and Hilditch [198] pointed out (i) that the combined yield of tetrahydroxystearic acids, m.p. 173° and 157°, like that of the crystalline tetrabromostearic acid, was of the same order from seed fat or from regenerated "α"-linoleic acid; (ii) that peracetic acid oxidation of linoleic acid gave small yields of the two tetrahydroxy-acids, m.p. 144° and 135° (obtained in an impure form, m.p. 126°), obtained by Nicolet and Cox; (iii) that regenerated "β"-linoleic acid gave only insignificant yields of the tetrahydroxy-acids, m.p. 173° and 157°, on alkaline oxidation; and (iv) that, after treatment with oxides of nitrogen, the partly isomerised "α"-linoleic acid gave only small yields of the latter tetrahydroxy-acids, but gave in addition traces of that of m.p. 144°. These workers concluded (i) that the linoleic acid of seed fats is confined to one geometrical isomeride; (ii) that the latter undergoes isomeric change during bromination or oxidation; (iii) that the "β"-linoleic acid is more than a mixture of other forms of $\Delta^{9,12}$-octadecadienoic acid and may include, in part, products which have undergone more profound modification than *cis-trans* isomerism; (iv) from the behaviour of "elaidinised" linoleic acid, that inability to afford the tetrahydroxystearic acids of m.p. 173° and 157° is not necessarily evidence of the absence of $\Delta^{9,12}$-octadecadienoic acids; and (v) from the behaviour of "α"-linoleic acid to acidic and alkaline oxidising agents, that the two pairs of isomeric tetrahydroxy-acids obtainable do not bear to each other the simple, inverse relationship apparent in the parallel case of oleic and elaidic, and their corresponding dihydroxystearic, acids.

In 1938 McCutcheon [203] reinvestigated and recapitulated the evidence for the tetrabromo- and tetrahydroxy-stearic acids obtained by different procedures from seed fat and regenerated "α"-linoleic acids but whilst concluding, as in the preceding instance, that the two pairs of tetrahydroxy-acid isomers bear no simple relationship to each other, he also held that the weight of evidence was still in favour of the existence of two geometrical isomers in the natural linoleic acid.

Brown and Frankel [192a] showed in 1938 that their maize oil linoleic acid, prepared by crystallisation from acetone at −70°, gave 96 per cent. of the yield of "α"-tetrabromostearic acid, m.p. 114°, given by regenerated "α"-linoleic acid; they conclude that seed fat and "α"-linoleic acids are identical. In later studies (1941, 1943) Brown *et al.*[192b] confirmed the identity of regenerated "α"-linoleic acid with the natural seed fat acid (except that the "α"-acid may contain up to 1 per cent. of conjugated acids); and stated that "β"-linoleic acid, obtained by debromination of the soluble, liquid tetrabromostearic acids, may contain from 15 to 53 per cent. of the *cis-cis*-acid, together with 32–70 per cent. of isomeric octadecadienoic acids and 6–22 per cent. of "much altered" acids. The isomeric acids contain no *trans-trans*-acid (since they give no tetrabromo-adduct, m.p. 78°) and are considered to be *cis* Δ^{9}-*trans* Δ^{12} and/or *trans* Δ^{9}*cis* Δ^{12}-octadecadienoic acids, except that they may contain from 2 to 6 per cent. of conjugated octadecadienoic acids. Brown and his colleagues consider that linoleic acids regenerated from the tetrabromo-adducts contain, even in the case of the "α"-acid, appreciable amounts of isomeric acids which they believe to be the result of isomerisation during the removal of bromine; such contaminating isomers can be segregated from the true "α"-(*cis-cis*) acid by low-temperature crystallisation of the latter.

Reimenschneider, Wheeler, and Sando [204] confirmed that only two tetrabromostearic acids (m.p. 115° and liquid) and only two tetrahydroxystearic acids (m.p. 174° and 163·5°) are obtainable from either natural, regenerated "α"-linoleic, or regenerated "β"-linoleic acids. They conclude that all three acids are stereochemically identical, in view of their findings that the yields of the crystalline tetrabromostearic acid from natural and "α"-linoleic acid were over 45 per cent. of the theoretical, whilst that from their "β"-linoleic acid was 36·7 per cent. It will be observed, however, that the yield of 36·7 per cent. of crystalline tetrabromostearic acid is much greater than that (24–25 per cent.) recorded by other workers (*vide infra*).

Kass and Burr[205] isomerised linoleic acid, with oxides of nitrogen[68] or with selenium,[74] and isolated from the product:

(i) A crystalline linoleic acid, m.p. 28–29°, which amounted to 16 per cent. or more of the whole product, gave an insoluble lead salt, yielded equal parts of a new crystalline tetrabromostearic acid, m.p. 78°, and of a liquid tetrabromostearic acid, and gave on oxidation a mixture of two tetrahydroxystearic acids, m.p. (sharp) 122° and 146° respectively;

(ii) A liquid isomeric linoleic acid, which was submitted to a lead salt separation in order to remove the crystalline isomeride still present (with about 5 per cent. of conjugated acid by-products). The liquid linoleic acid obtained from the soluble lead salts gave no crystalline tetrabromostearic acid, and on oxidation furnished two tetrahydroxystearic acids, one melting at 156–158° and the other at 126–127° (not identical with that of m.p. 122° above).

These authors point out that isomerisation of both ethenoid bonds in linoleic acid could produce two or all three of the remaining isomers, but that their data suggest that linoleic acid is either totally converted or is present in the product in quantities too small for detection by addition of bromine or by alkaline oxidation. They conclude that the original linoleic acid has been completely changed, but only into two of its possible isomerides (m.p. 28–29°, and a liquid form), and explain this by the assumption that the Δ^{9}-linkage may elaidinise alone, but that the Δ^{12}-bond cannot isomerise without the previous or simultaneous isomerisation of the Δ^{9}-bond.

According to Kass and Burr, therefore, the products of " elaidinisation " of linoleic acid will be solely *trans* Δ^{9}-*trans* Δ^{12}-octadecadienoic acid and *trans* Δ^{9}-*cis* Δ^{12}-octadecadienoic acid, and only the fourth possible member (*cis* Δ^{9}-*trans* Δ^{12}-octadecadienoic) of this group of acids remains to be isolated or characterised.

Contrary to the views of Brown and of some other workers, Kass and Burr believe that, although a polyethenoid fatty acid may form several isomeric bromo-adducts, no significant isomerisation occurs during debromination of any of the latter, at least in the non-conjugated series, and their later findings in the case of linolenic acid (*q.v.*) afford in their view further confirmation of this conclusion.

Hilditch and Jasperson[75] have re-examined the older observations, and also studied linoleic acid and its esters after isomerisation with selenium,[74] with the following chief results:

(*a*) The linoleic acid in unsaturated esters from cottonseed oil, and the regenerated " α "-linoleic acid from " α "-tetrabromostearic acid, give closely similar yields of the " α "-bromostearic acid, m.p. 114°, and the two tetrahydroxystearic acids, m.p. 173° and 157°.

(*b*) " α "-Linoleic acid gave 45 per cent., " β "-linoleic acid 24 per cent., and isomerised (Se) " α "-linoleic acid 0 per cent. yields of " α "-tetrabromostearic acid, m.p. 114°.

(*c*) On alkaline oxidation, " α "-linoleic acid gave 50 per cent., and " β "-linoleic acid 18 per cent. yields of the combined tetrahydroxystearic acids of m.p. 173° and 157°; isomerised (Se) " α "-linoleic acid gave only 2 per cent. yield of acid m.p. 155°, and no acid m.p. 173°.

(*d*) On alkaline oxidation, neither " α "- nor " β "-linoleic acids gave any tetrahydroxystearic acids m.p. 144° and 134°, but isomerised " α "-linoleic acid gave a combined yield of 18 per cent. of these acids.

Hilditch and Jasperson conclude (i) that " α "-linoleic acid and the natural seed fat linoleic acid are identical, and are the *cis* Δ^{9}-*cis* Δ^{12}-acid; (ii) that, on addition of bromine, this acid yields equal parts of tetrabromostearic acids corresponding with the *cis* Δ^{9}-*cis* Δ^{12}- and *cis* Δ^{9}-*trans* Δ^{12}-acids; (iii) that the " β "-tetrabromostearic acid reverts, on debromination, into an equal mixture of *cis* Δ^{9}-*cis* Δ^{12}- and *cis* Δ^{9}-*trans* Δ^{12}-acids, whilst the " α "-tetrabromostearic acid is not stereochemically altered during debromination; (iv) that it seems probable that isomerisation of a " α "-linoleic (*cis* Δ^{9}-*cis* Δ^{12}) acid by selenium at 220° results in almost complete conversion into the *trans* Δ^{9}-*trans* Δ^{12}-acid; and (v) that " β "-*linoleic acid* consists to a very large extent of $\Delta^{9,12}$-octadecadienoic acids.

The percentage yields of theory of tetrabromo- and tetrahydroxy-stearic acids recorded by Hilditch and Jasperson may be given for comparison in tabular form :

FROM :	TETRABROMO-STEARIC ACID M.P. 114°	TETRAHYDROXYSTEARIC ACIDS M.P. 173° M.P. 157°	M.P. 145° M.P. 134°
Natural linoleic acid (cottonseed oil)	50·3	48·7	nil
Regenerated " α "-linoleic acid	45·4	50·8	nil
Isomerised " α "- ,,	nil	1·7	18·6
Regenerated " β "- ,, *	23·9	18·2	nil
Isomerised " β "- ,,	nil	nil	4·1

It is evident that the results of these various studies, whilst in general agreement, vary in points of detail, both as regards factual observation and interpretation of the data obtained. There is now substantial agreement that the linoleic acid of seed fats is *cis* Δ^9-*cis* Δ^{12}-octadecadienoic acid, and also that addition of bromine to this acid causes the production of at least two stereochemically related tetrabromostearic acids. Much, however, remains to be understood with regard to the nature of the configurational changes which set in during addition of halogen, debromination of the bromo-adducts, oxidation, and geometric isomerisation.

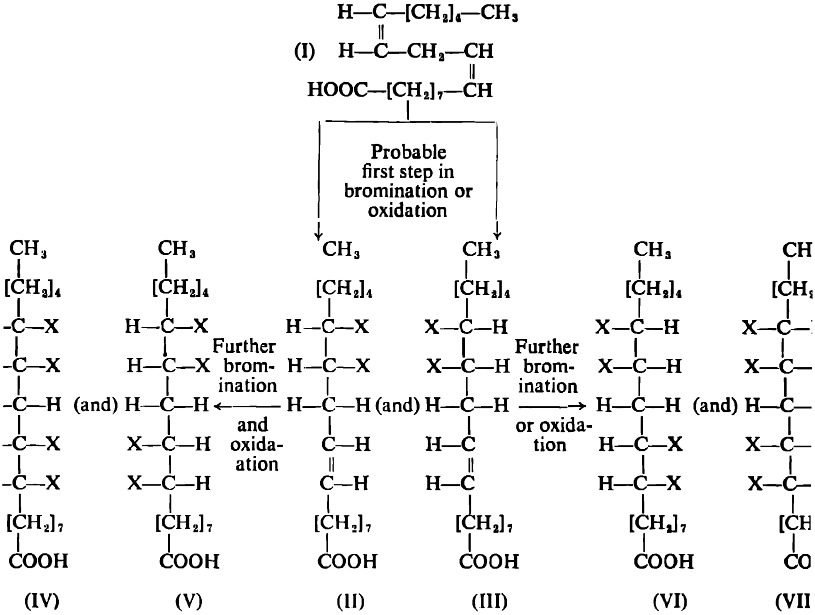
Whilst Kass and Burr consider that no isomeric changes accompany debromination with zinc, Brown and co-workers share with Hilditch and Jasperson the view that " β "-tetrabromostearic acid reverts in part both to " α "- and " β "-linoleic acids during debromination ; and Brown lays more emphasis than the other workers on the extent to which other isomeric (conjugated) by-products and " much altered " acids may also appear during debromination, especially in the case of the " β "-tetrabromostearic acid.

Again, arguing from the known fact that the Δ^9-octadecenoic acids reach an equilibrium in which about one-third of the *cis*- (oleic) form is still present, Hilditch and Jasperson assume that the Δ^9-bond in the dienoic acid is less likely to undergo geometric isomerisation than the Δ^{12}-bond, whereas Kass and Burr adopt the hypothesis that the Δ^9-bond is " elaidinised " preferentially to that in the Δ^{12} position.

The connection between the tetrahydroxystearic acids produced by oxidation under different conditions from the same or different isomeric forms of linoleic acid is also by no means wholly clear. An octadecadienoic acid should yield tetrabromo- or tetrahydroxy-stearic acids with four asymmetric carbon atoms, and therefore sixteen optically active or eight racemic possible forms. Unless Kass and Burr's four tetrahydroxy-stearic acids, m.p. 122°, 126–127°, 146° and 156–158° (p. 423) are all individual forms not identical with previously recorded isomers of similar melting-point, only four tetrahydroxy-stearic acids (m.p. 135°, 144°, 157° (or 163·5°) and 173°) have yet been produced from linoleic acid, and still fewer definite tetrabromostearic acids. Riemenschneider *et al.*[204] suggest, however, that only two racemic isomers (tetrabromo- or tetrahydroxy-derivatives) would

* Repeat experiments with " β "-linoleic acid gave 25·8, 21·4, and 21·4 per cent. yields of theory of the tetrabromostearic acid, m.p. 114°, and 17·7 per cent. yield of the combined tetrahydroxystearic acids of m.p. 173° and 157°. The higher yield (36·7 per cent.) of crystalline tetrabromostearic acid mentioned by Riemenschneider *et al.*[204] could not be duplicated ; Rollett [100] also records a yield of 26·2 per cent. of theory of the acid, m.p. 114°, from regenerated " β "-linoleic acid.

result from *cis*-addition, first to the Δ^{12}-linking, and then to the Δ^{9}-linking, of one form (e.g. the *cis* Δ^{9}-*cis* Δ^{12}-acid), according to the following scheme :


(I)
Probable first step in bromination or oxidation
Further bromination and oxidaation
Further bromination or oxidation
(and)
(IV)
(V)
(II)
(III)
(VI)
(VII

The end-products (IV) and VII) are optical isomers and constitute a racemate, whilst (V) and (VI) represent a second racemate.

Syntheses of linoleic and analogous acids. An unequivocal synthesis of linoleic acid has not yet been achieved, but Noller and Girvin [266] in 1937, starting from vinyl *n*-hexyl carbinol, $CH_3.[CH_2]_4.CH(OH).CH{:}CH_2$, prepared a mixture of bromides, $CH_3.[CH_2]_4.CHBr.CH{:}CH_2$ and $CH_3.[CH_2]_4.CH{:}CH.CH_2Br$, the mixed magnesium derivatives of which were condensed with 8, 9-dibromo-9-methoxynonyl chloride as in Noller and Bannerot's synthesis of oleic acid (p. 403). The mixture of octadecadienoic acids finally obtained contained some of the $\Delta^{9,12}$-octadecadienoic acids, since it furnished on oxidation small yields of the tetrahydroxystearic acids, but it gave no crystalline tetrabromostearic acid. It is evident, however, that little or none of the *cis-cis-* form of the acid would be expected to result from chemical synthesis.

Baudart [283b] has synthesised the *trans-trans*-$\Delta^{9,12}$-octadecadienoic acid, starting from 1, 2, 4, 5-tetrabromo-1, 5-diethoxypentane (prepared from glutaraldehyde diacetal). It was submitted to the Grignard reaction, first with magnesium *n*-amyl bromide and then with magnesium 6-methoxyhexyl bromide ; reduction of the final product with zinc in butyl alcohol gave 1-methoxy-$\Delta^{7,10}$-hexadecadiene, $CH_3.[CH_2]_4.CH{:}CH.CH_2.CH{:}CH.[CH_2]_5.CH_2(OCH_3)$. The methoxyl group was converted first into bromo-, and thence to the 1-iodohexadecadiene, which was condensed with malonic ester and sodium, giving a product which, on decarboxylation, furnished the $\Delta^{9,12}$-octadecadienoic acid which yields a tetrabromo-adduct, m.p. 77–78° (*cf.* p. 423).

Karrer and Koenig [267] have synthesised C_{19} and C_{20} dienoic acids from linoleic acid by converting its chloride with diazomethane into the corresponding ketone, R.CO.CHN_2, which on treatment with silver oxide in alcohol and subsequent hydrolysis gave $\Delta^{10,13}$-*nonadecadienoic acid.* The latter by a similar sequence of actions led to $\Delta^{11,14}$-*eicosadienoic acid.*

Other natural octadecadienoic acids (aquatic and animal fats). Although it was more or less tacitly assumed at one time that linoleic (or other octadecadienoic) acid accompanied oleic acid in fair quantity in fish and similar fats, there seems to be no record of the isolation of the characteristic tetrabromo- or tetrahydroxy-adducts of ordinary (seed fat) linoleic acid in these cases. Moreover, Green and Hilditch [206] showed that the unsaturated C_{18} acids of cod liver oil and whale oil consisted mainly of oleic with polyethenoid C_{18} (probably octadecatetraenoic) acids, and that octadecadienoic acids did not amount to more than about 10 per cent. of the unsaturated C_{18} group ; further, ordinary linoleic acid was not detected.

In cow milk fat, the absence of any but minute amounts of ordinary (seed fat) linoleic acid has been pointed out by Hilditch and Jones [207] (1929) and by Bosworth and Brown [106] (1933) and Eckstein [208] (1933). Green and Hilditch,[209] however, proved that the excess unsaturation over monoethenoid in butter fatty acids is due to octadecadienoic acids (probably other geometrical isomeric forms of seed fat linoleic acid) and this was confirmed by selenium isomerisation of butter unsaturated C_{18} acids by Hilditch and Jasperson,[210a] who also showed that no conjugated octadecadienoic acids are present in butter fat (see also Chapter III, p. 117). Later, these workers [210b] showed that the octadecadienoic acids of cow and goat milk fats are convertible on heating with alkali into conjugated forms (with spectrographically measurable absorption at 234 $m\mu$), and were thus able to determine the proportions present in these milk fats. Since these acids are neither the *cis* Δ^{9}-*cis* Δ^{12} nor the *trans* Δ^{9}-*trans* Δ^{12} forms, it would appear that they are either *cis* Δ^{9}-*trans* Δ^{12}- or *trans* Δ^{9}-*cis* Δ^{12}-octadecadienoic acid, or a mixture of both forms (*cf.* also J. B. Brown).

The liver and depot fats of oxen and sheep (and probably other similar animals) contain small quantities of C_{18} acids more unsaturated than oleic, which are for the most part octadecadienoic acids. They are similar to the corresponding cow milk fatty acids in their non-response to the tests for ordinary or seed fat linoleic acid, and are probably similar to the butter octadecadienoic acids in structure (see also Chapter III, pp. 88, 107) (Hilditch and Shorland,[133] and Longenecker [109]).

Other (artificially produced) octadecadienoic acids. (i) *Alkali isomerisation of linoleic acid.* T. Moore [268a] observed that, whilst natural linoleic and linolenic acids show only general absorption in the ultra-violet, the products obtained from these acids after prolonged heating with caustic alkali solutions give well-marked absorption bands owing to shifting of the double bonds and their rearrangement to conjugated di- or tri-ethenoid systems. Kass *et al.*[268b] confirmed this and showed that the conversion is rapid if the acids are heated with excess of alkali hydroxide at 180° or thereabouts in a high-boiling solvent such as ethylene glycol ; heating in strongly alkaline aqueous solution under pressure at 180° leads to the same result.[268c]

This process is of technical interest as a means of converting " drying " oils of the linseed type into oils possessing some of the characteristics of tung oil. It is also useful as a means of estimating linoleic and linolenic acids in mixtures of these with oleic and other fatty acids [269] (*cf.* Chapter IV, pp. 138, 154).

Kass *et al.*[268b] also found that reduction of methyl linoleate with sodium and alcohol leads to a mixture of $\Delta^{9,12}$- and $\Delta^{10,12}$-octadecadienols.

The mechanism of the reaction is probably dissociation of a hydrogen atom from the methylene group between two double bonds, leaving a system which by resonance is altered as follows:

$$-\mathrm{CH{:}CH.CH_2.CH{:}CH}-$$
$$\downarrow$$
$$-\mathrm{CH{:}CH.\dot{C}H.CH{:}CH}-$$
$$\swarrow\!\uparrow\!\searrow$$
$$-\mathrm{\dot{C}H.CH{:}CH.CH{:}CH}- \quad \text{and} \quad -\mathrm{CH{:}CH.CH{:}CH.\dot{C}H}-$$
$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad \downarrow$$
$$-\mathrm{CH_2.CH{:}CH.CH{:}CH}- \quad \text{and} \quad -\mathrm{CH{:}CH.CH{:}CH.CH_2}-$$

Both conjugated forms, $\Delta^{9,11}$- and $\Delta^{10,12}$-octadecadienoic acids, are present in the product.

(ii) *Dehydration of ricinoleic acid (castor oil).* When ricinoleic acid or its glycerides are heated at about 250° in presence of a suitable dehydrating catalyst, the elements of water are removed and a mixture of octadecadienoic acids is produced:

$$-\mathrm{CH_2.CH(OH).CH_2.CH{:}CH}-$$
$$\swarrow\!\mid\!\searrow$$
$$-\mathrm{CH{:}CH.CH_2.CH{:}CH}- \quad \text{and} \quad -\mathrm{CH_2.CH{:}CH.CH{:}CH}-$$

This process has been of interest to drying oil technologists since it was put forward by Scheiber,[270a] and has given rise to numerous patents. Formerly it was believed that the main product was the conjugated $\Delta^{9,11}$-acid,[270b] but more recent work by Bradley and Richardson, Forbes and Neville, and Priest and Mikusch [270c] has shown that $\Delta^{9,12}$-acids usually preponderate over the conjugated acid.

By alkali isomerisation (*cf.* above) of the octadecadienoic acids from dehydrated castor oil Mikusch [271] obtained a further mixture which contained about 20 per cent. of a $\Delta^{10,12}$-octadecadienoic acid, m.p. 57°, which yielded two tetrabromostearic acids melting at 150° and 104–105° and, on alkaline oxidation, a tetrahydroxystearic acid, m.p. 188°.

Conjugated diethenoid acid, $C_{19}H_{34}O_2$.

The peculiar acid which forms the greater part of the component acids of the seed fat of *Sterculia fœtida* and some other *Sterculia* species, the glycerides of which polymerise at 250° with considerable evolution of heat, was discussed in Chapter IV, p. 197. It contains 19 carbon atoms in the molecule and may be a 12-methyl-octadecadienoic acid; one ethenoid bond occupies the usual Δ^{9}-position, and a second ethenoid bond is almost certainly contiguous to the first, in the Δ^{11}-position.[277] This acid, as a component of seed fat, is therefore unique in more than one respect.

POLYETHENOID ACIDS WITH THREE OR FOUR DOUBLE BONDS (VEGETABLE FATS)

It is convenient to discuss the polyethenoid acids with more than two double bonds according to their occurrence in the vegetable or animal kingdoms, because the constitution of the acids is fundamentally different in the two categories in question.

In the vegetable kingdom, at the time of writing, polyethenoid unsaturation is almost wholly confined to acids of the C_{18} series, and the structure of the acids is generically similar to oleic, linoleic, or petroselinic acids in that they contain one or more of the groupings $=CH.[CH_2]_7.COOH$, $=CH.CH_2.CH=$, or $=CH.[CH_2]_4.COOH$. These acids can be further divided, however, into two sub-groups, depending upon whether they contain a conjugated unsaturated system.

(a) *Non-conjugated poly- (tri-) ethenoid acids,* $C_{18}H_{30}O_2$

cis-cis-cis-$\Delta^{9,12,15}$-**Octadecatrienoic (Linolenic) acid,** $CH_3.CH_2.CH:CH.CH_2.CH:CH.CH_2.CH:CH.[CH_2]_7.COOH$, is the most usual form of triethenoid C_{18} acid found in seed fats. It is, of course, most familiar from its occurrence in linseed oil, of the mixed fatty acids of which it forms 50 per cent. or more ; it also occurs in varying but appreciable proportions in most of the vegetable drying oils, notably perilla, hemp, pine seed, walnut seed, rubber seed, etc. It does not seem to have been recognised as a separate acid until Hazura isolated it in 1887.[211] Like linoleic acid, linolenic acid yields a mixture of crystalline and liquid or low melting hexabromostearic acids when treated with bromine.[212] The crystalline hexabromostearic acid (insoluble in ether) melts at 180–181° and on debromination again yields a linolenic acid which, on bromination, again furnishes both crystalline and liquid hexabromo-derivatives. The behaviour of linolenic acid in this respect is thus exactly parallel with that of linoleic acid, and the same arguments have been raised as to the implication of these results ; similarly, the crystalline hexabromostearic acid has frequently been taken to be derived from an "α-linolenic acid," that obtained from the remaining more soluble and lower melting hexabromo-derivatives being termed "β-linolenic acid." Erdmann, Bedford, and Raspe [213] submitted the ethyl linolenate obtained by debrominating the crystalline hexabromostearic acid to ozonisation and isolated propionaldehyde, malonic acid, and mono-ethyl azelate from the products of the reaction, which thus afforded proof of the structure of the acid ; this has been confirmed on several occasions by later workers,[214] and also by permanganate-acetone oxidation of partially hydrogenated methyl linolenate.[196]

Linolenic acid, when oxidised with alkaline permanganate, yields two hexahydroxystearic acids which have been termed respectively linusic (m.p. 203°) and *iso*linusic (m.p. 173–175°) ; the latter is more soluble in hot water than linusic acid.[215]

Shinowara and Brown [216] have shown that by crystallising an 8 per cent. solution of the mixed fatty acids of linseed or perilla oils in acetone at −20° and then at −45° (to remove saturated, oleic and as much linoleic acid as possible), and then further cooling the mother liquor from the last operation to −60° and −75°, crystals (11–13 per cent. of the original total acids) are obtained which contain about 75 per cent. of linolenic acid. Further repeated crystallisation of this product from dilute solutions in light petroleum at −55° to −65° gave crystal crops containing 85–88 per cent. of linolenic acid. These products gave similar, or slightly higher, yields of the crystalline hexabromostearic acid, m.p. 181°, compared with those obtained from regenerated "α"-linolenic acid prepared from the latter hexabromo-adduct.

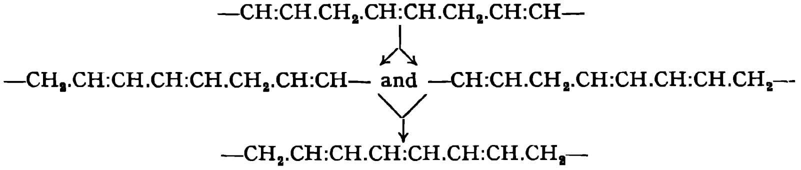
The purest linolenic acid obtained by low-temperature crystallisation by Brown *et al.*[192b] (1941) had iodine value 272·9 (theory 274·1) and melted at

11°. As stated previously (p. 422), Brown and his co-workers found that linolenic acid prepared from hexabromostearic acid, m.p. 181°, contained appreciable amounts of isomeric acids in addition to the *cis-cis-cis*-acid.

Daubert and Baldwin[278] have synthesised trilinolenin, which exists in dimorphic forms melting at —44·6° and —24·2°.

Kass and Burr[272] isomerised linseed oil fatty acids with selenium, and from the product obtained a crystalline hexabromostearic acid, m.p. 169–170°, which on debromination gave a solid form of linolenic acid (" elaido-linolenic " acid). This melts at 29–30° and, on rebromination, gave a 31 per cent. yield of the hexabromo-adduct, m.p. 169–170°. These authors state that the behaviour of the " unquestionably homogeneous elaidolinolenic acid " confirms their earlier conclusions that a polyethenoid acid may form several bromo-adducts and that no significant isomerisation occurs during debromination.

When seed fat linolenic acid is heated with excess of alkali hydroxide for a prolonged time in alcohol (T. Moore[268a]) or for a shorter time in butyl alcohol or ethylene glycol at their boiling points (Kass and Burr[268b]) isomerisation to conjugated acids sets in :



$$—CH:CH.CH_2.CH:CH.CH_2.CH:CH—$$

$$—CH_2.CH:CH.CH:CH.CH_2.CH:CH— \text{ and } —CH:CH.CH_2.CH:CH.CH:CH.CH_2—$$

$$—CH_2.CH:CH.CH:CH.CH:CH.CH_2—$$

In the products, acids with a conjugated diene system and one isolated ethenoid bond prodominate, but about 30 per cent. is completely isomerised to a conjugated triene acid. Whereas, however, linoleic acid yields both $\Delta^{9,\,11}$- and $\Delta^{10,\,12}$-octadecadienoic acids, the conjugated triene acid formed from linolenic acid appears to be wholly $\Delta^{10,\,12,\,14}$-octadecatrienoic acid, both external double bonds having shifted towards the central one (or, more accurately, a hydrogen atom having migrated from each active methylene group away from the central ethenoid group).

The conjugated triene acid melts at 79°, and on disruptive oxidation yields sebacic and butyric acids. It displays the characteristic absorption band in the ultra-violet spectrum at 268 mμ, with $E^{1\,\%}_{1\,\text{cm.}}$ about 1900. Use of the absorption spectrum of isomerised linolenic acid in the quantitative analysis of mixtures of unsaturated acids has already been referred to (*cf.* pp. 138, 154).[269]

The initial product of hydrogenation of linolenic acid (or linolenoglycerides) is, according to Lemon,[284a] mainly a $\Delta^{9,\,15}$-octadecadienoic acid, since it yields but little conjugated diene acid on treatment with alkali hydroxide at 180°. This acid, which may reach 18 per cent. of the total fatty acids in hydrogenated linseed oil, must be produced by preferential hydrogenation of the $\Delta^{12:13}$ double bond in the linolenic chain (see also K. F. Mattil,[284b] Bailey and Fisher[284c]).

$\Delta^{6,\,9,\,12}$-**Octadecatrienoic acid,** $CH_3.[CH_2]_4.CH:CH.CH_2.CH:CH.CH_2.CH:CH.[CH_2]_4.COOH$. This structural isomeride of ordinary linolenic acid has only been observed in the seed fat of *Œnothera biennis* (evening primrose), in which it was first noted by Heiduschka and Lüft.[217] It yields a hexabromostearic acid (m.p. 169°) and a hexahydroxystearic acid (m.p.

245°) ; Eibner, Widenmayer and Schild[150] have studied the oxidation products of this acid and find that the double bonds lie between the 6th and 7th, 9th and 10th, and 12th and 13th carbon atoms, so that the acid may be considered to have the same structural relation to petroselinic acid that ordinary linolenic acid has to oleic acid.

"Santalbic" acid, $C_{18}H_{30}O_2$, a solid acid forming nearly half of the seed fatty acids of *Santalum album*, melts at 41–42° and yields a liquid hexabromo-adduct. It is stated by Madhuranath and Manjunath[218] to be a non-conjugated octadecatrienoic acid of unknown structure.

(b) *Conjugated polyethenoid acids of the* C_{18} *series*

Up to the present, these include several, presumedly stereoisomeric, forms of $\Delta^{9,\,11,\,13}$-octadecatrienoic acid, a $\Delta^{9,\,11,\,13,\,15}$-octadecatetraenoic acid, and a keto-unsaturated acid, 4-keto-$\Delta^{9,\,11,\,13}$-octadecatrienoic acid.

$\Delta^{9,\,11,\,13}$-Octadecatrienoic (Elæostearic) acid, $CH_3.[CH_2]_3.[CH{:}CH]_3.[CH_2]_7.COOH$, occurs notably in China wood or tung oil, the seed fat of *Aleurites Fordii* and *montana*, of the mixed acids of which it forms 80–85 per cent. It has also been found in smaller proportions in some other seed fats, sometimes accompanied by 4-keto-elæostearic acid ; its distribution, as known at the present time, appears from Table 51 (pp. 166–168) in Chapter IV.

The acid present in the natural oil ("α-elæostearic acid," m.p. 48–49°) is transformed by the action of light into a solid crystalline isomeride, m.p. 71° ("β-elæostearic acid"). The change from the "α" to the "β"-geometrical isomeride is much more rapid and complete than the "elaidin" reaction of acids with only one ethenoid bond or with two or more isolated ethenoid bonds. It is promoted not only by light, but also by traces of iodine and other substances, and it also probably occurs when the "α"-acid or its esters are heated above 150°–200°. Both forms of the acid show characteristic absorption bands in the ultra-violet at 268 mμ, with $E^{1\%}_{1\,\mathrm{cm.}}$ 1800–2000.

Oils containing elæostearic glycerides, and the acid itself or its esters, possess the characteristic property of "gelation" (i.e. setting to a solid rubber-like mass) when submitted to the action of heat. The acid contains a conjugated system of three double bonds and for this reason it does not react normally with solutions such as those of Wijs or Hanus ; consequently it was for a long time considered to be a di-ethylenic acid, but the work of Böeseken, Steger and van Loon, and others[219] on the molecular refractivity of the acid, the amount of hydrogen absorbed in order to effect complete conversion into stearic acid, and on modified methods of iodine absorption, have demonstrated clearly that it contains three ethylenic linkages and that these are almost certainly conjugated. These facts, taken in conjunction with Majima's[220] study of the products of ozonisation of the acid, in which he isolated *n*-valeric aldehyde, *n*-valeric acid and azelaic acid, fully establish the structural formula of the acid. This formula was further confirmed by Eibner and Rossmann,[221] who obtained glyoxal in 60 per cent. yield from the ozonide of the acid, but observed no succinic aldehyde ; whilst the absorption spectra of the acid and its esters show, according to Manecke and Volbert,[222] that it is not isomeric with linoleic acid and must contain more than two double linkings. Morrell and Marks[223] have studied in great detail the decomposition products of the substances formed when elæostearic acid or its esters combine with atmospheric oxygen, and their work incidentally affords further confirmation of the correctness of the structure assigned to the acid.

Morrell and Samuels[224] have shown that the α- and β- forms of elæostearic acid give different addition compounds with maleic anhydride in the Diels-Alder reaction (m.p. respectively 62·5° and 77°) ; these addition products, on oxidation with potassium permanganate and acetone yield (i) in the case of the product from the α-acid, azelaic acid and a brown tar and (ii) in the case of the β-acid, valeric acid, and a similar tar. From this and other oxidation data it is evident that, in the α-acid, combination with maleic anhydride occurs at the 11th and 14th carbon atoms, whereas in the β-acid the addition takes place at the 9th and 12th carbon atoms. These experiments may therefore indicate that the difference between the α- and β-acids consists in different configurations (e.g. *cis-cis-trans-* and *trans-cis-cis-*) of the unsaturated groups.

It may be mentioned here that Myers, Kass, and Burr[273] found that the relative rates of absorption of oxygen at 40° by various triethenoid acids (mols. oxygen per mol. acid in 100 minutes) were as follows: "α"-elæostearic acid ($\Delta^{9,11,13}$) 2·68, "β"-elæostearic acid ($\Delta^{9,11,13}$) 1·02, $\Delta^{10,12,14}$-octadecatrienoic acid 0·64, and seed fat linolenic acid 0·52.

Other naturally occurring geometrical isomerides of α-elæostearic acid. Several other acids have been reported as stereoisomeric forms of α-elæostearic acid within recent years, but some of these have been shown later to differ from this acid. Two rare acids, punicic and trichosanic, are at present however accepted as other forms of $\Delta^{9,11,13}$-octadecatrienoic acid which are geometrically isomeric, but not identical, either with the natural α-elæostearic acid or with the β-elæostearic acid into which the α-acid is converted by the action of light, etc.

Punicic acid, m.p. 44°, was first observed by Toyama and Tsuchiya[225] in pomegranate seed oil in 1935, and its structure as another stereoisomeric form of α-elæostearic acid has been confirmed by Farmer and van den Heuvel.[226]

Trichosanic acid, m.p. 35–35·5°, was similarly observed by Toyama and Tsuchiya[225] in the seed fat of *Trichosanthes cucumeroides* ; Kaufmann, Baltes, and Büter[227] state that the mixed fatty acids contain 29 per cent. of trichosanic acid.

Both punicic and trichosanic acids pass by isomerisation into β-elæostearic acid.

4-Keto-$\Delta^{9,11,13}$-octadecatrienoic (α-Licanic) acid, $CH_3.[CH_2]_3.[CH:CH]_3.[CH_2]_4.CO.[CH_2]_2.COOH$, is at present unique amongst natural fatty acids in containing a ketonic group. It is present in large amounts in Brazilian oiticica oil (formerly regarded as the seed oil of *Couepia grandiflora*, but now known (Holdt[228]) to be that of *Licania rigida*). It was first reported by Willborn[229] in 1931 who, from the supposed source of the fat, termed it couepic acid. Under this name it was also examined by van Loon and Steger,[230] who stated that it melted at 74–75° and considered that it was a geometrical isomeride of α- and β-elæostearic acid. In 1935, however, Brown and Farmer[231] showed that the acid contained a keto-group, and re-named it licanic acid. They found that, although complete hydrogenation of licanic acid leads to the production of stearic acid, the first main product of hydrogenation is 4-ketostearic acid (m.p. 96·5°). Brown and Farmer established the constitution of the natural (α-) licanic acid by oxidation; natural or α-licanic acid melts at 74–75° (semicarbazone, m.p. 110–111°), and passes by the action of light in presence of traces of iodine or sulphur into a β-licanic acid, m.p. 99·5° (semicarbazone, m.p. 138°). The maleic anhydride adducts formed from the licanic acids and corresponding glycerides have been studied by Morrell and Davis.[232]

$\Delta^{9, 11, 13, 15}$**-Octadecatetraenoic (Parinaric) acid,** $CH_3.CH_2.[CH{:}CH]_4.[CH_2]_7.COOH$, m.p. 85–86°, was discovered by Tsujimoto[233] in 1933 in "akarittom" fat, the seed fat of *Parinarium laurinum*; he named it parinaric acid, stated that it yielded a "β-parinaric" acid, m.p. 95–96°, by the action of light in presence of traces of iodine, and believed that it was a further stereoisomeride of elæostearic acid. Farmer and Sunderland,[234] however, showed that it contained a conjugated system of four, and not three, double bonds, and proved that its constitution was that given above. Its absorption spectrum is very similar to that of decatetraene (Kaufmann *et al.*[235]). At present this is the only known instance of a vegetable fat tetra-ethenoid acid. Other species of *Parinarium*, moreover, yield seed fats with elæostearic and linoleic acids (*P. macrophyllum*), or licanic and elæostearic acids (*P. Sherbroense*), but contain none of the C_{18} tetraene acid.

The occurrence of the $\Delta^{9, 11, 13, 15}$-octadecatetraenoic acid in the seed fat of the Japanese balsam (*Impatiens balsamina*) has however been reported by Tutiya.[274]

POLYETHENOID ACIDS WITH THREE, FOUR, FIVE OR SIX DOUBLE BONDS (MAINLY IN FATS OF AQUATIC ORIGIN)

So far as fats from aquatic sources are concerned, a fundamental difference in their polyethenoid acids is that the latter belong to the C_{16}, C_{18}, C_{20}, C_{22}, and C_{24} series and not, as in vegetable fats, only to the C_{18} series. C_{16}, C_{18}, and C_{24} polyethenoid acids are, however, not very abundant in marine animal fats, whereas those of the C_{20} and C_{22} series frequently form a considerable proportion (e.g. 30–40 per cent.) of the total acids of a marine fatty oil. These highly unsaturated acids were first reported in 1906, under the name of clupanodonic acid, by Tsujimoto,[236] who at that time believed it to be an acid of the C_{18} series but, in 1920, noted that its formula was $C_{22}H_{34}O_2$ (docosapentaenoic). In the meantime it had become recognised that unsaturated acids of both the C_{20} and the C_{22} series were commonly present in fish oils and that possibly, in each series, acids ranging from tri- to hexa-ethenoid might be present.

At this point we may leave the marine fats for a moment, in order to point out that similar acids, notably arachidonic (eicosatetraenoic), $C_{20}H_{32}O_2$, had also been recognised as present in small quantities in the liver and other organ fats, and sometimes in traces in the depot fats, of land animals such as the ox and pig. Brown and Deck[237] observed about 0·4 per cent. of arachidonic acid in pig depot fats in 1930, and Brown and Sheldon[237] detected traces of the same acid in beef fats in 1934, whilst Brown also isolated it from the fatty acids of ox brain (1931). Ault and Brown[237] (1934) showed that it formed over 20 per cent. of the fatty acids of ox adrenal phosphatides, and Shinowara and Brown[237] later (1940) obtained methyl arachidonate in 90–95 per cent. purity by crystallisation of the methyl esters of ox adrenal phosphatide acids from acetone at low temperatures, followed by fractional distillation. Mowry, Brode, and Brown[237] showed in 1942 from the absorption spectrum that this arachidonic acid contains little if any conjugated unsaturated acid, but on heating with excess of alkali it is isomerised similarly to linolenic acid (*q.v.*) and develops the absorption bands characteristic for the conjugated polyene acids; a solid isomeride, m.p. 95–98°, was isolated from the isomerised products. These authors, and also Smedley-MacLean *et al.*,[275] have proved from the products of ozonolysis of the methyl arachidonate of adrenal phosphatides that the acid is $\Delta^{5,8,11,14}$-eicosatetraenoic acid.

Brown restricts the polyethenoid acids of all land animal fats to this single form; but other workers suggest that both C_{20} and C_{22} acids may be present in these land animal fats (Hilditch, Lea, and Pedelty,[110] pig depot fats; Riemenschneider, Ellis, and Titus,[238] egg yolk fats).

As regards the polyethenoid acids of the C_{20} and C_{22} series present in marine animal fats, considerable uncertainty has existed as to their constitution, although it has been known for some time that they are derived from the normal or straight-chain aliphatic acids. When hydrogenated, they furnish respectively *n*-eicosanoic (arachidic) and *n*-docosanoic (behenic) acids,[117] the straight-chain structure of these products having been verified by X-ray analysis (Morgan and Holmes [32]). Various structures have been assigned, chiefly by Toyama and Tsuchiya and by Tsujimoto, as a result of studies of the oxidation products from fractions of the various acids obtained, as a rule, by processes of ester distillation involving somewhat lengthy exposure to temperatures of 200° and above. It now seems probable, in the light of the work of Farmer and van den Heuvel [239] (*vide infra*), that changes occur when these acids or their esters are heated at or above 200° for any length of time, whilst it has also become evident that excessive heating with alcoholic alkali causes cyclisation to set in at some point in the polyethenoid chain (Edisbury *et al.*[240]). The possible isomerisation and polymerisation of polyethenoid acids and esters (from cod liver oil) as the result of heat and other factors involved during analysis has also been studied by Burr *et al.*[276] They found that exposure to heat during fractional distillation in a vacuum has no effect on mono-, di-, or tri-ethenoid acids or their esters, but that both isomerisation and polymerisation may take place with more unsaturated acids; they found that much more isomeric change goes on during hydrolysis with hot alkali solutions than by exposure to heat alone.

Farmer and van den Heuvel's important contribution [239] consisted in separation of the highly unsaturated acids of cod liver oil by repeated passage of their methyl esters through the "molecular still," wherein evaporation from thin films (rather than distillation) is carried out at extremely low pressures. By this procedure the highest temperature attained by the esters does not exceed 120° and any one time of exposure of any one portion of the esters to this temperature is less than two minutes. As a result, these investigators separated the polyethenoid esters into homologous groups with the following average number of ethenoid linkings per molecule C_{16} 1·3, C_{18} 2·7, C_{20} 4·9, and C_{22} 6. (The low values for the C_{16} and C_{18} acids are due to mono-ethenoid acids remaining unseparated from the polyethenoid derivatives in the course of the preliminary lithium salt separation from acetone.) From considerations of refractivity and hydrogen (iodine) value Farmer and van den Heuvel showed that similar acids obtained, by themselves or other workers, by the ordinary processes of ester-fractionation had undergone a partial loss of unsaturation (by cyclisation); and it now appears that the polyethenoid acids of marine animal oils possibly only include one member in each homologous group, with the following numbers of ethenoid linkings: C_{16} 3, C_{18} 4, C_{20} 5, C_{22} 6, and C_{24} 6.

Farmer and van den Heuvel [239] also showed that the docosahexaenoic acid $C_{22}H_{32}O_2$ is structurally homogeneous, non-conjugated, and yields *n*-docosanoic (behenic) acid on hydrogenation. From its oxidation products they deduced that it contained four :CH.CH_2.CH: groups and one :CH.$[CH_2]_2$.CH: group between the terminal groups CH_3.CH: and :CH.$[CH_2]_2$.COOH. It is therefore one of the following five possible acids :

DOCOSAHEXAENOIC ACID:

$\Delta^{4,8,11,14,17,20}$ $CH_3.CH[:CH.CH_2.CH]_4:CH.[CH_2]_2.CH:CH.[CH_2]_2.COOH$

$\Delta^{4,7,11,14,17,20}$ $CH_3.CH[:CH.CH_2.CH]_3:CH.[CH_2]_2.CH:CH.CH_2.CH:CH.[CH_2]_2.COOH$

$\Delta^{4,7,10,14,17,20}$ $CH_3.CH[:CH.CH_2.CH]_2:CH.[CH_2]_2.CH[:CH.CH_2.CH]_2:CH.[CH_2]_2.COOH$

$\Delta^{4,7,10,13,17,20}$ $CH_3.CH:CH.CH_2.CH:CH.[CH_2]_2.CH[:CH.CH_2.CH]_3:CH.[CH_2]_2.COOH$

$\Delta^{4,7,10,13,16,20}$ $CH_3.CH:CH.[CH_2]_2.CH[:CH.CH_2.CH]_4:CH.[CH_2]_2.COOH$

It has at all events become clear that there is fundamental dissimilarity between the polyethenoid marine animal fatty acids and corresponding acids belonging to the vegetable kingdom or, for that matter, oleic and hexadecenoic acids themselves. In nearly all the polyethenoid (C_{18}) vegetable acids yet known the grouping :CH.$[CH_2]_7$.COOH occurs, whilst this is also present in oleic, linoleic, and hexadecenoic acids. It is true that the chain :CH.CH_2.CH:, characteristic of linoleic and linolenic acids, evidently occurs also in the polyethenoid marine animal fatty acids, but another, which is extremely rare in the vegetable fatty acids, is also prominent, namely, :CH.$[CH_2]_2$.CH:.

The first evidence of the presence of this 4-carbon chain fragment in the fish oil acids is due to Tsujimoto,[241] who showed in 1928 that a " clupanodonic " acid ($C_{22}H_{34}O_2$) fraction isolated from Japanese sardine oil yielded, on ozonisation, succinic acid, COOH.$[CH_2]_2$.COOH, in amount up to 49 per cent. of the weight of clupanodonic acid oxidised.

The absence, in the polyethenoid C_{20} and C_{22} marine animal fatty acids, of any conjugated double linkings was demonstrated by Morrell and Davis,[242] who found that neither the acids nor their esters gave crystalline adducts with maleic anhydride.

It was mentioned earlier that Japanese investigators have applied the method of oxidation by ozone to many of the individual polyethenoid acids which they have isolated from fish oils. It must be borne in mind, in view of Farmer and van den Heuvel's observations, that some of these products may represent partly cyclised or altered acids instead of the polyethenoid acid originally present in the fish fats. Subject to this reservation, a list is given of the acids (belonging to the C_{16}, C_{18}, C_{20}, C_{22}, C_{24}, and C_{26} series) whose constitution has been given by these workers :

		NAMED	STRUCTURE	FAT	INVESTIGATORS
$C_{16}H_{23}O_2$	Hexadeca*trien*oic	Hiragonic	$\Delta^{6,10,14}$	Sardine (body)	Toyama and Tsuchiya [243]
$C_{16}H_{24}O_2$	Hexadeca*tetraen*oic		$\Delta^{4,8,11,14}$ or $\Delta^{4,9,12,15}$	,,	Tutiya [274]
$C_{18}H_{30}O_2$	Octadeca*trien*oic		not given	,,	,, [274]
$C_{18}H_{28}O_2$	Octadeca*tetraen*oic	Moroctic	$\Delta^{4,8,12,15}$	,,	Toyama and Tsuchiya [243]
$C_{20}H_{32}O_2$	Eicosa*tetraen*oic		$\Delta^{4,8,12,16}$	,,	,, ,, [243]
$C_{20}H_{30}O_2$	Eicosa*pentaen*oic		$\Delta^{4,8,12,15,18}$	,,	,, ,, [243]
$C_{22}H_{34}O_2$	Docosa*pentaen*oic	Clupanodonic	$\Delta^{4,7,11,15,19}$ or $\Delta^{4,8,11,15,19}$	,,	Tsujimoto [241]
			$\Delta^{4,8,12,15,19}$	,,	Toyama and Tsuchiya [243]
$C_{22}H_{32}O_2$	Docosa*hexaen*oic	Clupanodonic	$\Delta^{4,8,12,15,18,21}$ or* $\Delta^{4,8,11,14,17,20}$	,,	,, ,, [243]
$C_{24}H_{36}O_2$	Tetracosa*hexaen*oic	Nisinic	$\Delta^{4,8,12,15,18,21}$	,,	,, ,, [243]
$C_{26}H_{42}O_2$	Hexacosa*pentaen*oic	Shibic	Not given	Tunny liver	Ueno and Yonese [244]
$C_{26}H_{40}O_2$	Hexacosa*hexaen*oic	Thynnic	,, ,,	,, ,,	,, ,, [244]

* Identical with one of Farmer and van den Heuvel's possible alternative structures.

No statements are given as to the proportions of C_{24} and C_{26} acids present in the oils concerned, but it may be taken for granted that they represent very minor components of the total fatty acids.

Baudart [282] found that the unsaturated C_{20} and C_{22} acids of the liver oil of a shark species (*Carcharodon Carcharias*) contained small proportions of $\Delta^{11,14}$-eicosadienoic, of $\Delta^{11,14}$-docosadienoic acids, $C_{20}H_{36}O_2$ and $C_{22}H_{40}O_2$, of $\Delta^{8,11,14}$-eicosa- and docosa-trienoic acids, $C_{20}H_{34}O_2$ and $C_{22}H_{38}O_2$, and of $\Delta^{8,12,16,20\ (\mathrm{or}\ 10)}$-docosatetraenoic acid, $C_{22}H_{36}O_2$.

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CHAPTER X

SYNTHETIC GLYCERIDES: INDIVIDUAL NATURALLY OCCURRING FATTY ALCOHOLS AND ACYL ETHERS OF GLYCEROL

THE individual acidic components of fats were discussed in Chapter IX, and it remains to give in the present chapter similar information concerning the alcoholic components of the lipids, which fall into four main groups:

(*a*) Glycerol, the trihydric alcohol characteristic of the true fats (triglycerides). This is, of course, by far the most important in relation to the fundamental part which it bears in the fats themselves, but its properties and reactions are so well known that it is unnecessary to deal with the subject here. Its chief interest, as regards the natural fats, lies in the innumerable mixed triglycerides of the fatty acids which can be derived from it, and accordingly the first part of this chapter is occupied by a brief review of the work which has been carried out up to the present in the synthesis and characterisation of triglycerides of known configuration, simple or mixed, of the higher fatty acids.

It may be noted, in passing, that under certain conditions of fermentative rancidity the glycerol of natural fats is converted to some extent into trimethylene glycol,[1] $CH_2(OH).CH_2.CH_2(OH)$.

(*b*) Higher alcohols of the normal aliphatic series corresponding with the various natural higher fatty acids, which occur as the alcoholic components of the waxes (wax esters); some of the latter accompany glycerides, others (mainly of higher molecular weight than the previous class) occur alone in the form of plant (cuticle) or insect waxes, etc.

(*c*) Three mono-alkyl ethers of glycerol, known as chimyl, batyl, and selachyl alcohols (ethers of glycerol with one molecule of, respectively, hexadecyl, octadecyl, or octadecenyl alcohols) occur as fatty esters in some marine animal fats, especially the liver oils of some Elasmobranch fish.

(*d*) The sterols or polycyclic alcohols of high molecular weight; and also vitamin A (related to the carotenoid group). These compounds, although they occur in combination with fatty acids as esters to quite a large extent, are of course not aliphatic in nature, and are so complex in structure that their study forms a separate field of organic chemical research in itself.

For this reason, the constituents of what is usually termed the "unsaponifiable matter" which may accompany natural fats (sterols and vitamin D, carotenoids and vitamin A, squalene and other hydrocarbons of high molecular weight) are not dealt with in detail in this book.*

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* Recent monographs on these groups of compounds include:

F. L. Fieser, "Chemistry of Products related to Phenanthrene" (2nd Ed., 1937).

E. Friedmann, "Sterols and Related Compounds" (1937).

A. Winterstein and K. Schön, "Die Sterine," Hefter-Schönfeld "Fette und Fettprodukte," Vol. I (1936).

H. von Euler, "Carotin und Vitamin A" (1932).

P. Karrer and H. Wehrli, " 25 Jahre Vitamin-A-Forschung " (1933).
A. Winterstein and C. Funk, " Vitamine," Klein's " Handbuch der Planzenanalyse " (1933).
L. Zechmeister, " Die Carotinoide " (1934).
L. Zechmeister, " Lipochrom und Vitamin A," Hefter-Schönfeld " Fette und Fettprodukte," Vol. I (1936).
T. P. Hilditch, "Squalen," Hefter-Schönfeld "Fette und Fettprodukte," Vol. I (1936).

SYNTHETIC GLYCERIDES *

The problem of the structural configuration of glycerides is of great importance and has attracted many workers in the field of fat chemistry, but much remains to be done before decisive information becomes available upon the configuration of the major component glycerides occurring in natural fats. The difficulties which have retarded the work in this particular direction are primarily lack of reliable data in the case of naturally occurring glycerides, due (i) to the extreme difficulty in isolating individual glycerides from a mixture (*cf.* the studies of Klimont, Bömer, Amberger, and others, Chapter V, pp. 225–227), and (ii) to unreliable data recorded in the literature for synthetic glycerides ; the latter has arisen chiefly from the use of impure materials, and inherent difficulties encountered in the synthetic methods adopted. A further factor introducing uncertainty is that of the polymorphism of glycerides, a factor which probably accounts to a large extent for the wide ranges in melting points recorded for individual glycerides. Thus Grün and Schacht [2] record 32°, 36·5°, and 39·5° for the transition and melting points of symmetrical β-myristodilaurin whereas McElroy and King [3] record 50·2° for the same compound.

The subject matter here discussed will be of the nature of a brief account of the main advances in the study of synthetic glycerides, chronological order being maintained wherever possible.

Although the nature of the natural fats was understood by Chevreul [4] in 1823, there appears to be no record of an attempt to synthesise glycerides until Berthelot [5] prepared tristearin in 1853. On heating quantities of glycerol and stearic acid for 20 hours at 200° C. he obtained a compound melting at 61 ° crystallising from solvents in nodules, and this he believed to be monostearin. Heating the same mixture for 114 hours at 100° a product melting at 58° was obtained and this was believed to be distearin. Tristearin was obtained by heating monostearin with 15 to 20 times its weight of stearic acid, and on recrystallisation the product was shown to possess all the properties of naturally occurring tristearin.

Although the possible existence of mixed triglycerides was postulated by Berthelot, it was not until 1887 that Wynter Blyth and Robertson [6] obtained a solid glyceride from butter fat which they identified as an oleo-butyropalmitin.

With the realisation of the fact that in general naturally occurring fats consisted of mixtures of mixed triglycerides, a large number of mono-, di-, and tri-glycerides were synthesised by Guth [7] in an endeavour to formulate a scheme of identification. α-Monoglycerides were prepared by heating equivalent quantities of α-monochlorohydrin and the sodium salt of a long-chain fatty acid at 110° for 4 hours. In this way α-monostearin of melting point 73° was obtained, but later work by Malkin and Shurbagy [8] indicates that the melting points recorded by Guth were those of an unstable lower-melting form or that this method of synthesis is incapable of giving a pure product.

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* This section of Chapter X has been contributed by M. L. Meara, Ph.D, (Bristol), A.R.I.C.

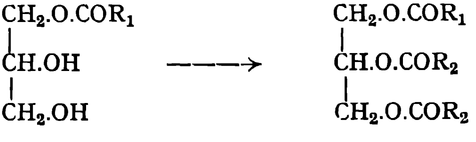
The αα′-diglycerides were prepared by heating αα′-dichlorohydrin with sodium salts, whereas " αβ-diglycerides " were obtained from αβ-dibromohydrin. In the light of later work (*v. infra*) these " αβ-diglycerides " must in reality have been αα′-diglycerides. Unsymmetrical α-stearodipalmitin was then prepared by heating α-monostearin with palmitic acid under reduced pressure, whereas the symmetrical isomer (β-stearodipalmitin) was obtained in like manner from stearic acid and αα′-dipalmitin. Slight differences in the crystalline form of the isomers were recorded but both apparently melted at 60°. It is highly probable that these glycerides contained as impurity small amounts of simple triglycerides, since it has been shown [9] that in the synthesis of palmitodiolein by heating together palmitic acid and αα′-diolein definite small quantities of tripalmitin are formed.

Guth did not record more than one melting point in the case of the mixed triglycerides, but studied the problem of polymorphism in the case of tristearin for which melting points at 56° and 71° had been observed. He showed that a specimen of well crystallised tristearin had only one melting point, 71°, and pointed out that the same melting point was obtained on keeping the specimen some time before re-observing the melting point. It was suggested that the melted and rapidly cooled substance was behaving as a supercooled liquid, which, on being disturbed solidified to its original state but that the latent heat thus set free was sufficient to melt the whole if the quantity were small.

In 1903 Grün [10] devised a new synthesis for αα′-diglycerides via glyceryl disulphate, but showed that poor yields were obtained in the case of the lower members. These were later converted into symmetrical mixed triglycerides, and under suitable conditions two forms were isolated, it being possible to convert the unstable to the stable modification by inoculation with a little of the latter. This observation was of considerable importance since it showed not only the physical existence of these forms, but also that Guth's hypothesis was untenable.

One of the most important advances in glyceride chemistry was that due to Fischer [11] and co-workers, who showed beyond all doubt that no deductions as to the structure of the resulting glycerides could be made in their formation from halohydrins and sodium salts. In order to synthesise glycerides of known constitution, isopropylidene glycerol, the structure of which had been determined by Irvine, MacDonald and Soutar,[12] was employed. This was esterified with acid chloride in the presence of pyridine or quinoline, the resulting complex being hydrolysed to α-monoglyceride by shaking with cold concentrated hydrochloric acid. In this way α-monoglycerides of a high degree of purity were prepared.[13]

It was found that treatment of an α-monoglyceride with acid chloride gave rise to a mixed triglyceride in good yield.

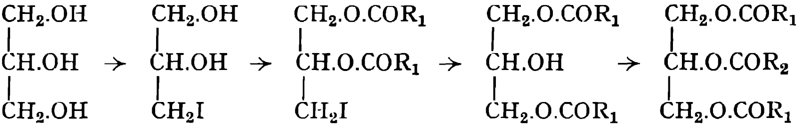


$$\begin{array}{l} CH_2.O.COR_1 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} \longrightarrow \begin{array}{l} CH_2.O.COR_1 \\ | \\ CH.O.COR_2 \\ | \\ CH_2.O.COR_2 \end{array} \qquad (I)$$

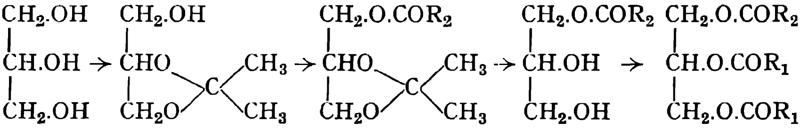
If α-iodohydrin, $CH_2(OH).CH(OH).CH_2I$, were treated in a similar manner a diacyl iodohydrin would be formed which might be expected to have given an αβ-diglyceride on partial hydrolysis. This on treatment with $R_1.COCl$ would give rise to the glyceride (I) (above), but it was found that the isomer of higher melting point and lower solubility was obtained, indicating that migration of an acyl group from a β- to an α-carbon atom had taken place during the reaction. With the establishment of the possibility of migration of acyl groups from β- to α-carbon atoms in the glycerol molecule, it was realised that many of the earlier syntheses of alleged β-mono- and αβ-diglycerides were invalid, but it appears to have been left to Fairbourne[14, 15, 16] and his collaborators to re-investigate the syntheses systematically in the light of the newer work.

In 1929 King and collaborators[17, 18, 3] began an extensive research on the properties of synthetic glycerides, Fischer's methods, illustrated diagrammatically below, being adopted.

(a) *Symmetrical mixed triglycerides*



(b) *Unsymmetrical mixed triglycerides*



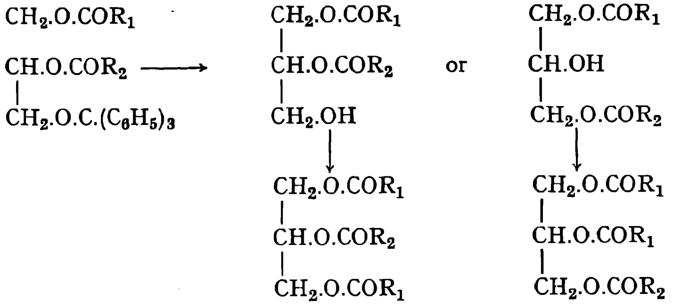
The general conclusions drawn from their work were :

(1) The symmetrical isomer of any given pair had a higher melting point, higher refractive index, and lower solubility than the unsymmetrical compound.

(2) An increase in the length of the second fatty acid chain present increases the melting point and refractive index.

These were found to hold for saturated acids from C_6 to C_{14}, except that palmito- and stearo-dilaurins had lower melting points than that of myristodilaurin, a similar irregularity occurring in the lower members of the distearin series. It is unfortunate that these workers failed to take into consideration the possibility of polymorphism occurring in their synthesised glycerides.

Another method for the synthesis of glycerides of known constitution was devised in 1935 by Verkade and co-workers,[21] who developed the use of triphenylmethyl (" trityl ") derivatives of glycerol which had previously been studied by Helferich and Sieber.[22] By the action of triphenylchlormethane a triphenylmethyl (" trityl ") group was introduced into the glycerol molecule before esterification (the " trityl " group, it had been found, could later be easily and quantitatively removed). It was shown that the triphenylmethyl derivative obtained by partial esterification with an acyl chloride, $R_1.COCl$, followed by a second acyl chloride, $R_2.COCl$, was different from that obtained by using the acid chlorides in the reverse order, indicating that the triphenyl group must be associated with a primary alcoholic group. Partial hydrolysis to the diglyceride followed by further esterification with $R_1.COCl$ should give either the symmetrical or unsymmetrical mixed triglyceride according to whether migration had occurred or not:



$$\begin{array}{l} CH_2.O.COR_1 \\ CH.O.COR_2 \\ | \\ CH_2.O.C.(C_6H_5)_3 \end{array} \longrightarrow \begin{array}{c} \begin{array}{l} CH_2.O.COR_1 \\ | \\ CH.O.COR_2 \\ | \\ CH_2.OH \end{array} \\ \downarrow \\ \begin{array}{l} CH_2.O.COR_1 \\ | \\ CH.O.COR_2 \\ | \\ CH_2.O.COR_1 \end{array} \end{array} \quad \text{or} \quad \begin{array}{c} \begin{array}{l} CH_2.O.COR_1 \\ | \\ CH.OH \\ | \\ CH_2.O.COR_2 \end{array} \\ \downarrow \\ \begin{array}{l} CH_2.O.COR_1 \\ | \\ CH.O.COR_1 \\ | \\ CH_2.O.COR_2 \end{array} \end{array}$$

The experimental production of the unsymmetrical glyceride is clear proof of migration, although later work [23] has shown that the removal of the triphenylmethyl group by catalytic hydrogenation gives rise to an αβ-diglyceride. Further, a ditriphenylmethyl glyceride gives rise on catalytic hydrogenation to a β-monoglyceride.

A full account (with full literature references) of the work of Verkade, Helferich and their collaborators and others on the preparation of mono- and di-" trityl "-glycerides and the use of the latter in the synthesis of mixed glycerides of known configuration has been published by Verkade.[24]

Simple saturated triglycerides. The simple triglycerides were systematically reinvestigated in 1934 by Clarkson and Malkin,[19] whose method of synthesis was essentially that due to Sheij,[20] which can for convenience be called a " direct synthesis " method.

It was shown that under suitable conditions the simple triglycerides could exist in three modifications, a stable (β) form in which the long chains are inclined with respect to the planes formed by the terminal methyl groups, a less stable monotropic (α) form in which the chains are vertical, and a third form which is not truly crystalline, possessing properties which are usually associated with a glass.

In this study X-ray investigation confirmed the existence of the two crystalline forms since two distinct types of long and side spacings were obtained.

TABLE 99. *MELTING POINTS, TRANSITION POINTS, AND X-RAY LONG SPACINGS OF THE SIMPLE TRIGLYCERIDES*

No. of C Atoms in Acid	T.P.	M.P. (°C.)		Long Spacings (Å).	
	Glass	α	β	α	β
C_{10}	−15	18	31·5		26·8
C_{11}	1·0	26·5	30·5	33·0	29·6
C_{12}	15	35·0	46·4	35·6	31·2
C_{13}	25	41·0	44·0	37·7	34·1
C_{14}	33	46·5	57·0	41·2	35·8
C_{15}	40	51·5	54·0	42·9	38·9
C_{16}	45	56·0	65·5	45·6	40·6
C_{17}	50	61·0	63·5	48·5	43·5
C_{18}	54·5	65·0	71·5	50·6	45·0

Side Spacings (Å) of the Simple Triglycerides

β form even acids	3·7	3·9	4·6	5·3
,, ,, odd ,,	3·65	4·0	4·6	5·3
α form and glass	4·2			

TABLE 100. *MELTING POINTS OF THE SYMMETRICAL MIXED TRIGLYCERIDES*

	CAPRO				LAURO				MYRISTO				PALMITO				STEARO			
	GLASS	α	β′	β	GLASS	α	β′	β	GLASS	α	β′	β	GLASS	α	β′	β	GLASS	α	β′	β
Dicaprin					6	25	34	37·5(*a*)	3	21	30	34(*a*)	6	27	36	40(*a*)	5	34	40	44·5(*a*)
Dilaurin	8	23 30·8(*b*)	33	38·5(*a*)					24	37 50·2(*b*) 32, 36·5, 39·5 } (*c*)	44	48(*a*)	19	35 47·0(*b*)	42·5	45·5(*a*)	21	38 45·6(*b*) 37·5, 42·5 } (*c*)	43	47(*a*)
Dimyristin	16	37	40	43·5(*a*)	24	35 49·5(*d*) 46·5(*c*)	45	50(*a*)					38	49 59·8–60(*d*) 49·5(*e*)	55	58·5(*a*)	33	47	53	55·5(*a*)
Dipalmitin	20	42 66·0(*d*)	48	51·5(*a*)	34	47 63·5–64(*d*) 54·6(*e*)	50	53·5(*a*)	37	46 58·5–59(*d*)	55	60(*a*)					49	59 64·8(*d*) 60(*b*) 69·5(*g*)	65	68(*a*)
Distearin	30	47 56·2(*h*)	53	57(*a*)	36	52 59·8(*h*) 52·5, 56·5, 58·5 } 56·5, 66·5 } (*c*)	58	60·5(*a*)	47	56 63·5(*h*) 55·5, 57 } 57, 65 } (*c*)	59	62·5(*a*)	50	56 68·0(*h*) 52·5, 63 } (*i*) 67, 63·3 } (*g*)	64	68(*a*)				

For references ("(*a*)", etc.), see Table 101.

TABLE 101. *MELTING POINTS OF THE UNSYMMETRICAL MIXED TRIGLYCERIDES*

	CAPRO				LAURO				MYRISTO				PALMITO				STEARO			
	GLASS	α	β′	β	GLASS	α	β′	β	GLASS	α	β′	β	GLASS	α	β′	β	GLASS	α	β′	β
Dicaprin					0	17·5	26	30(*a*)	3	20	31	34·5(*a*)	2	24	32	35(*a*)	10	32	38	41(*a*)
Dilaurin	5	26	31 32·6(*b*)	35·5(*a*)					19	33·5	39 42·8(*b*) 41 ⎫ (*c*) 36·5 ⎭	43·5(*a*)	20	33	43 44·8(*b*) 47–48(*i*)	46·5(*a*)	20	31	41·5 45·4(*d*) 44 ⎫ (*c*) 46 ⎭	45(*a*)
Dimyristin	15	32	38	43·5(*a*)	22	37	42 48·5(*d*)	46·5(*a*)					34	45·5	50·5 53·0(*d*) 47·8(*e*)	54(*a*)	36	46	52	56(*a*)
Dipalmitin	23	37	41 60(*d*)	45·5(*a*)	32	45	49·5 54·5(*d*) 53·5(*e*)	54(*a*)	36	47·5	52 55·5(*d*)	57(*a*)					46·5	55	59·5 63·5(*g*) 60(*f*)	62·5(*a*)
Distearin	33	42·5	46 48·2(*h*)	49(*a*)	36	47	52 50·6(*h*) 50·9(*d*) 49–50(*i*) 52·5 ⎫ (*c*) 49·5 ⎭ 49 ⎫ (*c*) 47 ⎭	—(*a*)	44	54	57·5 58·5(*h*) 62 ⎫ 59 ⎬ (*c*) 52 ⎭	62(*a*)	50	57	61 62·6(*h*) 63·2(*g*)	65(*a*)				

(*a*) Malkin and collaborators.[28]
(*b*) McElroy and King.[3]
(*c*) Grün and collaborators.[3]
(*d*) Averill, Roche, and King.[17]
(*e*) Heiduschka and Schuster.[26]
(*f*) Guth.[7]
(*g*) Amberger and Bromig.[27]
(*h*) Robinson, Roche, and King.[18]
(*i*) Fischer, Bergmann, and Bärwind.[13]

Mixed saturated triglycerides. In the light of the experience gained in the examination of the simple triglycerides Malkin and co-workers[8, 26] next examined the α-monoglycerides, αα′-diglycerides, symmetrical and unsymmetrical mixed triglycerides of the saturated series. The α-mono- and αα′-di-glycerides were found to resemble the simple triglycerides in existing in three polymorphic forms, whereas the symmetrical and unsymmetrical mixed triglycerides were shown to exist in four forms, two of which have tilted chains, one a vertical rotating chain, the fourth being a vitreous form. The melting points obtained are compared with those obtained by other workers in Tables 100 and 101 (pp. 448, 449). It is seen that in many cases it should be possible to distinguish between symmetrical and unsymmetrical isomers, but it must also be borne in mind that in general the isolation of an individual glyceride from a natural fat is a very difficult task, and that the synthetic work has shown that even a trace of impurity causes the non-appearance of the stable crystalline modification, a form which is extremely difficult to produce in the case of the higher members even when their purity is of a high order.

X-ray examination has shown that frequently the differences in long spacings between symmetrical and unsymmetrical isomers lie near the limit of experimental error, but that detectable differences in side spacings, even though they may be small in some cases, serve to distinguish between pairs of isomers.

TABLE 102. *X-RAY LONG SPACINGS (Å) OF SYMMETRICAL AND UNSYMMETRICAL MIXED TRIGLYCERIDES*

	SYMMETRICAL			UNSYMMETRICAL		
	α	β′	β	α	β′	β
Caprodilaurin	—	—	30·0	—	30·4	31·8
Laurodimyristin	39·6	36·7	34·7	—	35·3	36·5
Myristodipalmitin	44·4	42·4	39·0	43·9	40·3	41·5
Palmitodistearin	50·5	47·5	44·2	48·8	44·7	46·5
Laurodicaprin	—	—	29·0	—	—	28·4
Myristodilaurin	—	34·5	33·6	—	34·5	33·0
Palmitodimyristin	45·0	39·7	38·1	42·8	39·5	37·7
Stearodipalmitin	50·2	44·7	43·2	47·8	43·9	42·5
Caprodimyristin	—	33·7	52·5	—	33·8	35·2
Laurodipalmitin	44·6	77·0	59·0	43·4	38·5	39·8
Myristodistearin	49·5	44·7	65·8	48·5	43·4	45·0
Myristodicaprin	—	30·3	46·5	—	31·3	47·5
Palmitodilaurin	—	36·6	35·5	—	36·2	54·6
Stearodimyristin	44·0	41·0	40·0	46·4	41·7	61·4
Caprodipalmitin	39·0	74·0	56·5	—	74·1	56·2
Laurodistearin	47·1	42·4	63·7	47·4	42·8	—
Palmitodicaprin	—	—	49·5	—	—	49·7
Stearodilaurin	40·8	37·5	56·8	—	38·7	57·0
Caprodistearin	—	76·3	61·2	73·7	—	60·0
Stearodicaprin	—	—	51·6	—	5·10	52·6

TABLE 103. *X-RAY SIDE SPACINGS (Å) OF SYMMETRICAL AND UNSYMMETRICAL MIXED TRIGLYCERIDES*

		SYMMETRICAL	UNSYMMETRICAL
Caprodilaurin	(β)	3·79 4·35 4·62 5·33	(β) 3·67 3·86 4·60 5·35 (β′) 3·83 4·18 4·35 (same for the four compounds)
Laurodimyristin	(β)	3·84 3·89 4·61 5·34	
Myristodipalmitin	(β)	3·74 3·86 4·61 5·34	
Palmitodistearin	(β)	3·68 3·86 4·61 5·34	
	(β′)	3·82 4·05 4·16 4·35 same for above four compounds)	
Laurodicaprin	(β)	3·87 4·17 4·39	(β) 3·67 3·86 4·60 5·35 (β′) 3·83 4·18 4·35 (same for these four compounds)
Myristodilaurin	(β)	3·85 4·06 4·26 4·45	
,,	(β′)	3·85 4·35	
Palmitodimyristin	(β)	3·81 4·13 4·31	
,,	(β′)	3·88 4·13 4·31	
Stearodipalmitin	(β)	3·81 4·03 4·20 4·48	
,,	(β′)	3·81 4·35	
Caprodimyristin	(β)	3·98 4·22 4·39	(β) 3·72 3·90 4·53 4·67 5·40 (β′) 3·78 4·09 4·26 4·50 (same for all three compounds)
Laurodipalmitin	(β)	3·84 4·28 4·62 5·28	
Myristodistearin	(β)	3·74 4·09 4·41	
	(β′)	3·82 4·11 4·28 (same for above three compounds)	
Myristodicaprin	(β)	3·90 4·30 4·60	(β) 3·84 4·60 4·84 5·21 (β′) 3·78 4·09 4·26 (same for these three compounds)
,,	(β′)	3·86 4·60 5·24	
Palmitodilaurin	(β & β′)	3·86 4·09 4·29	
Stearodimyristin	(β & β′)	3·86 4·20 4·39	
Caprodipalmitin	(β)	3·84 4·61 5·32	(β) 3·84 4·60 4·85 5·26 (β′) 3·82 4·18 4·35 (β) 3·84 4·60 4·85 5·26 (β′) 3·82 4·18 4·35
,,	(β′)	3·84 4·08 4·31	
Laurodistearin	(β)	3·84 4·61 5·32	
,,	(β′)	3·84 4·08 4·31	
Palmitodicaprin	(β)	3·86 4·59 4·90 5·34	(β) 3·84 4·60 4·85 5·26 (β′) 3·94 4·35
Stearodilaurin	(β & β′)	3·83 4·02 4·20 4·41	(β) 3·84 4·60 4·85 5·26 (β′) 3·86 4·11 4·35
Caprodistearin	(β)	3·86 4·61 5·34	(β) 3·74 4·02 4·33 4·60
,,	(β′)	3·83 4·11 4·39	
Stearodicaprin	(β)	3·72 3·87 4·24 4·58 4·90 5·29	(β) 3·84 4·60 5·30 (β′) 3·80 4·10 4·35

The side spacing associated with the α-form is invariably a single line situated at 4·19 Å.

✓ **Simple unsaturated triglycerides.** So far no reference has been made to glycerides containing unsaturated acids. Until recently relatively little work had been done on these, an investigation by Carter and Malkin [29] representing the first comprehensive study of unsaturated triglycerides. They obtained the following data for certain simple tri-unsaturated glycerides:

	M.P. °C.				X-RAY (LONG SPACINGS Å)		
	GLASS	α	β′	β	α	β′	β
Trielaidin	15·5	37	—	42·0	—	—	44·1
Trierucin	6	—	25	30·0	—	54·7	51·1
Tribrassidin	43	50	—	59	59·3	—	53·6

The side spacings of the β-forms of tribrassidin and trielaidin are the same as those of the simple triglycerides, namely, 3·7, 3·9, 4·6, 5·3 Å, whereas trierucin exhibits a unique group of side spacings at 3·70, 3·84, 4·03, 4·60, 5·24 Å, for the β-form, and a typical group for the β′ form at 3·88, 4·07, 4·28, 4·53 Å.

Triolein and trilinolein were synthesised by Wheeler, Riemenschneider, and Sando [30] by direct esterification with glycerol, and purified by distillation in a molecular still. Subsequently, Daubert and Baldwin [31] prepared α-monolinolein, α-monolinolenin, trilinolein, and trilinolenin. The following melting points were recorded by these workers for the stable (β, I) and lower melting (α, II ; III) forms of these glycerides :

	III	II (α)	I (β)
Triolein [30]	−32°	−12°	+ 5°
Trilinolein [30]	—	−43	−13
Trilinolein [31]	—	−45·6	−12·9
Trilinolenin [31]	—	−44·6	−24·2
α-Monolinolein [31]	—	−22·8	+12·3
α-Monolinolenin [31]	—	13·5	+15·7

To overcome the difficulty that unsaturated fatty acids yield acid chlorides of doubtful purity when treated with thionyl chloride (*cf.* below), Black and Overley [32] developed a new synthesis of glycerides from the acid chlorides of the bromine addition products of unsaturated fatty acids, followed by subsequent removal of the halogen to yield unsaturated glycerides of known configuration. In addition to monotetrabromostearin and monolinolein (m.p. 14–15°), these workers prepared tritetrabromostearin, from glycerol and tetrabromostearoyl chloride in chloroform in the presence of quinoline. This compound was crystalline and melted sharply at 81·0–81·5° ; on debromination with zinc and alcohol it gave trilinolein, m.p. −5 to −4°. Rebromination of the acids obtained after saponification of the synthetic monolinolein and trilinolein gave rise to the usual 50 per cent. of tetrabromostearic acid, m.p. 115·5°.

Mixed saturated-unsaturated triglycerides. Daubert, Longenecker, and and co-workers [33] have now synthesised a considerable number of mixed saturated-unsaturated glycerides by methods essentially those evolved by Fischer, Bergmann, and Bärwind.[13] Oleyl chloride was prepared in 90 per cent. yield by refluxing oleic acid with oxalyl chloride ; this avoids the side reactions consequent upon the use of thionyl chloride with unsaturated acids. The melting points of these glycerides have been recorded together with the melting points of their fully hydrogenated derivatives ; the latter are compared with those of the corresponding synthetic saturated mixed triglycerides (Tables 104A and 104B). At present the thermal properties of the polymorphic forms in which these glycerides, like the saturated mixed triglycerides, are known to be capable of existing, have been investigated only in the case of the symmetrical and unsymmetrical oleo-disaturated and unsymmetrical monosaturated di-oleo glycerides, by the methods developed so successfully by Malkin and co-workers for the thermal investigation of the saturated α-mono- and αα′-di- simple and mixed symmetrical and unsymmetrical tri-glycerides.

TABLES 104A AND 104B. *MELTING POINTS OF THE SATURATED-UNSATURATED MIXED TRIGLYCERIDES*

A. MONO-OLEO DISATURATED GLYCERIDES

	SYMMETRICAL				Fully hydrogenated	
	IV	III	II	I	Found	Reported
β-Oleo-dicaprin	−16·4°	−10·2°	0·6°	6·2°	45·0°	44·5°
β-Oleo-dilaurin	−7·5	+1·4	11·0	16·5	51·5	50·9
β-Oleo-dimyristin	+2·1	12·3	21·5	26·3	56·0	55·5
β-Oleo-dipalmitin	12·0	20·8	30·4	35·2	68·0	68·0
β-Oleo-distearin	22·3	27·8	37·0 to 37·6	41·6	71·5	71·5

	UNSYMMETRICAL				Fully hydrogenated	
	IV	III	II	I	Found	Reported
α-Oleo-dicaprin	−27°	−15°	−2·5°	5·3°	44·0°	41·0°
α-Oleo-dilaurin	−15·5	−10	+4·8	15·5	45·2	45·4
α-Oleo-dimyristin	+3·8	+18·6	22·7	25·0	57·0	56·0
α-Oleo-dipalmitin	18·5	29·8	—	34·5	63·0	62·6
α-Oleo-distearin	26·7	—	—	38·5	—	—

B. UNSYMMETRICAL MONOSATURATED DIOLEOGLYCERIDES

				Fully hydrogenated	
	IV	III	I	Found	Reported
α-Caproyl-diolein	−56·5°	−34·2°	−14·5°	44·0°	42·7°
α-Caprylo-diolein	−50·0	—	−18·5	47·5	47·6
α-Capro-diolein	−40·5	−16·5	−0·6	47·8	48·2
α-Lauro-diolein	−32·0	−10·9	+4·3	49·7	50·6
α-Myristo-diolein	−21·8	−4·2	13·3	58·2	58·5
α-Palmito-diolein	−13·2	+2·5	15·8	62·3	62·6
α-Stearo-diolein	−1·5	8·6	22·9	—	—

Daubert [33] has also given the following data for the melting points of α-mono-elaido-disaturated glycerides and α-monosaturated-dielaidins, and of the products produced from each by complete hydrogenation :

	M.P.	Fully hydrogenated M.P.
α-Elaido-dicaprylin	3·0°	32·0°
α-Elaido-dicaprin	15·0	41·0
α-Elaido-dilaurin	27·0	45·5
α-Elaido-dimyristin	39·5	56·0
α-Capro-dielaidin	25·0	49·0
α-Lauro-dielaidin	35·5	54·0
α-Myristo-dielaidin	40·0	62·5

Daubert and Baldwin [33] have reported the melting points of synthesised α-linoleodisaturated and α-monosaturated dilinoleoglycerides as follows :

	M.P.
α-Linoleo-dicaprylin	−13 to −12°
α-Linoleo-dicaprin	−1 to 0
α-Linoleo-dilaurin	+15–16
α-Linoleo-dimyristin	20–21
α-Linoleo-dipalmitin	26–27
α-Linoleo-distearin	32–33
α-Lauro-dilinolein	−12 to −11°
α-Myristo-dilinolein	−9 to −8
α-Palmito-dilinolein	−4 to −3
α-Stearo-dilinolein	+5 to +6

Synthesis of optically active mono-, di-, and tri-glycerides, and of other optically active glycerol derivatives. A remarkable series of optically active derivatives of glycerol has been synthesised by H. O. L. Fischer, E. Baer, and their students.[34] They prepared in the first instance *d*- and *l*-acetonylglycerols [34a] by oxidising 1,2,5,6-diacetonyl *d*- (or *l*-) mannitol with lead tetra-acetate, and hydrogenating the acetonyl-*d*- (or *l*-)

glyceraldehyde so obtained to *d*- (or *l*-) acetonyl-glycerol ($[\alpha]_D \pm 12{\cdot}6°$). From these they prepared various acylated derivatives, which on removal of the acetone complex yielded optically active monoglycerides * ; for example :

l-α-Monoglycerides [34b]

	M.P.	$[\alpha]_D$
Lauryl	53–54°	−3·8°
Palmityl	71–72	−4·4
Stearyl	76–77	−3·6
p-Nitrobenzoyl	88–89	−17·1

Conversion of these optically active monoglycerides into unsymmetrical mixed triglycerides, however, led to the startling result that when all three acyl substitutes were long-chain aliphatic acids, the optical rotatory power disappeared, although with aromatic derivatives it persisted :

Mixed Triglycerides from l-α-Monoglycerides [34b]

	M.P.	$[\alpha]_D$
l-α-Lauro-β,α′-distearin	48·5°	0·0°
l-α-Palmito-β,α′-dilaurin	44	0·0
l-α-Stearo-β,α′-dipalmitin	62·5	0·0
l-α-(*p*-Nitrobenzoyl)-β,α′-distearin	67·5	−1·4
l-α-(*p*-Nitrobenzoyl)-β,α′-dibenzoin	88	−19·9

It has thus been made clear that, in the mixed triglycerides of higher aliphatic acids, lack of observable rotatory power may occur in an enantiomorphic form of a molecule which possesses asymmetry. This leads to the possibility (already discussed in Chapter VI, p. 272) that natural asymmetric triglycerides, although optically inactive, are not necessarily racemic.

By other reactions, Baer and Fischer also produced optically active α,β-dipalmitin and α,β-distearin,[34c] and, in a different group of compounds, synthesised the optically active α-glycerol ethers of *n*-hexadecyl and *n*-octadecyl alcohols,[34d] which were found to be identical with the naturally occurring chimyl and batyl alcohols (*cf.* this chapter, p. 459). The rotatory power of the diacetyl derivative of the synthetic α-glycerol *n*-octadecyl ether was $[\alpha]_D -7{\cdot}6°$ (in chloroform).

Finally, commencing from *d*- or *l*-acetonylglycerol, the corresponding *l*- and *d*-α-glycerophosphoric acids were prepared [34e] ; the *l*-acid was shown to be identical with the glycerophosphoric acid produced during alcoholic fermentation or glycolysis, and also present in phosphatides. From *l*-α-monobenzoylglycerol ($[\alpha]_D -16{\cdot}8°$) Baer, Cushing, and Fischer succeeded in preparing a typical *mono-phosphatidic acid* (although not of the aliphatic series), *l*-α-benzoyl-β-glycerophosphate, $[\alpha]_D +9°$. Baer and Fischer [34] have pointed out some biochemical conclusions to be drawn from these configurational studies, especially in regard to the transformation of hexosediphosphate during fermentation into triose phosphoric acids, the occurrence of *l*-α-glycerophosphoric acid alike during hexose fermentation and in natural phosphatidic acids and phosphatides, and the probability that *l*-α-glycerophosphoric acid plays an important part in the transformation of carbohydrate into fat in the animal body, thus supplying the asymmetry necessary for the synthesis of optically active α-phosphatides, and also optically active fats, in nature.

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* It should be noted that steric considerations cause the production of *l*-monoglycerides from *d*-acetonylglycerol, and conversely ; this apparent change of configuration is due only to the peculiar asymmetry, centred around the β-carbon atom, of the glyceraldehyde-glycerol series, and does not involve a "Walden" inversion.

NATURALLY OCCURRING HIGHER ALIPHATIC ALCOHOLS

The chief higher fatty alcohols present in lipids dealt with in this book are cetyl (*n*-hexadecyl), *n*-octadecyl, and *n*-tetradecyl alcohols in the saturated series and oleyl (*n*-Δ^9-octadecenyl) alcohol in the unsaturated series; these correspond respectively in carbon content and in chemical constitution with palmitic, stearic, myristic, and oleic acids. Other alcohols, saturated and unsaturated, of the C_{12}, C_{20}, C_{22}, and C_{24} series are also occasionally encountered, whilst in the true (ester-) waxes of plants and insects the characteristic alcohols are members of the saturated series of still higher (e.g. C_{26} to C_{36}) carbon content ("ceryl," "melissyl," etc., alcohols).

It may be pointed out that, artificially, any of these natural alcohols can be prepared from the corresponding acids, or the esters of the latter, by two methods:

(i) Reduction of fatty acid esters in solution in absolute alcohol or butyl alcohol with sodium (Bouveault and Blanc [35]):

$$R.COOC_2H_5+2H_2=R.CH_2OH+C_2H_5OH.$$

In this way all the alcohols from octadecyl, $C_{18}H_{37}(OH)$, to pentacosyl, $C_{25}H_{51}(OH)$, were prepared from the corresponding acids by Levene and Taylor [36] in the course of their syntheses of the normal saturated fatty acids containing from 19 to 26 carbon atoms; whilst cetyl, tetradecyl, dodecyl, oleyl, and probably other alcohols of this group have been obtained from the corresponding fatty acid esters by the same means at various times by different workers.

(ii) Hydrogenation of glycerides, simple esters or the free fatty acids themselves at 200 atmospheres pressure and about 200° in presence of reduced basic copper chromate (" copper chromite " catalyst).[37] This process is now used extensively for the technical production of various higher fatty alcohols.

Direct syntheses of " even-number " higher alcohols up to $C_{18}H_{37}(OH)$ have also recently been effected by the hydrogenation of polyene aldehydes prepared by condensation of crotonaldehyde (Kuhn [38]).

SATURATED HIGHER *n*-ALIPHATIC ALCOHOLS

The group of alcohols of intermediate molecular weight occurring in natural lipids (mainly in certain marine animal oils) includes *n*-dodecanol (*n*-dodecyl, lauryl alcohol), m.p. 24–26°; *n*-tetradecanol (*n*-tetradecyl, myristyl alcohol), m.p. 39°; *n*-hexadecanol (*n*-hexadecyl, cetyl alcohol), m.p. 50°; *n*-octadecanol (*n*-octadecyl, stearyl alcohol), m.p. 59°; and *n*-eicosanol, m.p. 71°. The alcohols of higher molecular weight, which occur as esters of acids of similar molecular size in plant cuticle waxes, bees and other insect waxes, etc., are mixtures of alcohols with even numbers of carbon atoms from C_{24} to C_{36}. Usually a somewhat complex mixture of these compounds, inseparable by methods at present available, is present; but occasionally in some leaf waxes one particular alcohol is present to the virtual exclusion of all others. A very comprehensive study of the alcohols of plant and insect waxes was carried out by Chibnall *et al.*,[39] who reached the conclusions given in the preceding sentences. These investigators point out that the use in the literature of such terms, for example, as ceryl or melissyl alcohol for, respectively, the alcohols $C_{26}H_{53}(OH)$ and $C_{30}H_{61}(OH)$ is misleading, since the natural products referred to under these names are almost invariably mixtures of the even-numbered homologues. They propose that a large number of names of this nature should be abandoned, and that the mixtures which they represent should be referred to as such (e.g. $C_{26}+C_{28}+C_{30}$ alcohols, etc.).

The following notes may be added with reference to the distribution in nature of some of the higher *n*-aliphatic alcohols:

n-**Dodecanol,** $CH_3.[CH_2)_{10}.CH_2(OH)$, was reported in porpoise (*Tursiops truncatus*) head and jaw oils by Gill and Tucker,[40] but Lovern [41] was unable to confirm this observation. Ueno and Koyama [42] have stated that traces of this alcohol, and also of *n*-decanol and *n*-octanol, occur in the alcohols of sperm blubber oil.

n-**Tetradecanol,** $CH_3.[CH_2]_{12}.CH_2(OH)$, occurs as a minor component (about 8 per cent.) in the wax esters of sperm head oil (André and François,[43] Hilditch and Lovern [44]), and also in the head oil of the porpoise (Lovern [41]).

n-**Hexadecanol,** cetyl alcohol, $CH_3.[CH_2]_{14}.CH_2(OH)$, was observed by Chevreul [45] about 1817 in sperm head oil, in which it forms about 45 per cent. of the total higher alcohols (André and François,[43] Hilditch and Lovern [44]). Tsujimoto,[46a] and also Toyama,[46b] stated in 1925 that it was a constituent of the alcohols of Arctic sperm blubber oil. Hilditch and Lovern [44] found about 25 per cent. of cetyl alcohol in sperm blubber alcohols, and Lovern [41] observed 60 per cent. of cetyl alcohol in the alcohols of porpoise (*Phocæna communis*) head oil. The occurrence of much cetyl alcohol in the body fat of a tropical deep-sea fish, the castor-oil fish (*Ruvettus pretiosus*), has been recorded by Cox and Reid,[47] and in the body fat of *Ruvettus tydemani* and the ovary fat of the grey mullet, *Mugil Japonicus*, by Tsujimoto and Koyanagi.[46c]

n-**Octadecanol,** $CH_3.[CH_2]_{16}.CH_2(OH)$, is present in small quantities in sperm head [43, 44] and blubber oils [44, 46b] and probably also in porpoise and dolphin blubber oils,[41] but in any of these it probably does not amount to more than 5 per cent. of the total alcohols present.

n-**Eicosanol,** $CH_3.[CH_2]_{18}.CH_2(OH)$, is possibly present in minute amounts in the oils mentioned in the preceding cases, but has not been definitely isolated therefrom. It has been found in waxes present in certain dermoid cysts.[48]

"Even-number" normal alcohols from $C_{26}H_{53}(OH)$ to $C_{36}H_{73}(OH)$. The following details are included in the paper by Chibnall *et al.*[39] referred to previously:

n-**Hexacosanol,** $C_{26}H_{53}(OH)$, m.p. 79·5°, is almost the only higher alcohol constituent in the wax from blades of cocksfoot grass, and the same statement holds for *n*-**Octacosanol,** $C_{28}H_{57}(OH)$, m.p. 83·4°, in the wax of wheat blades, and for *n*-**Triacontanol,** $C_{30}H_{61}(OH)$, m.p. 86·5°, in lucerne leaf wax. Of other plant cuticle waxes, apple cuticle wax alcohols are a mixture of C_{26}, C_{28}, and C_{30}, carnauba wax alcohols include all the "even-number" alcohols from C_{26} to C_{34} (especially the higher members), candelilla, and also cotton, wax alcohols range from C_{28} to C_{34}.

In the insect waxes the mixture of "even-number" alcohols appears frequently to be still more complex. Beeswax alcohols range from C_{24} to C_{34}, those of lac wax from C_{26} to C_{36}. Cochineal wax appears to be unusual in containing 15-keto-*n*-tetratriacontanol, $CH_3.[CH_2]_{18}.CO.[CH_2]_{13}.CH_2(OH)$, as its chief component alcohol.*

UNSATURATED HIGHER ALIPHATIC ALCOHOLS

In the group of marine animal oils (notably those of the sperm whales and the porpoise family) in which wax esters accompany glycerides, unsaturated as well as saturated alcohols are present; the unsaturated members recorded range from C_{10} to C_{22}. In the unusual seed wax of *Simmondsia californica* the alcohols present are mono-ethenoid C_{20} and C_{22} compounds.

cis Δ^{9}-*n*-**Octadecenol (oleyl alcohol)**, $CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7.CH_2(OH)$, is the most important of the unsaturated group, and is the most abundant higher alcohol component of sperm head and blubber oils and porpoise blubber oils. It was apparently first definitely recognised by Tsujimoto [49, 46a] and by Toyama [50, 46b] in certain shark oils and also in sperm oils. Both authors state that the greater part of the alcohols present in the body oils of the ordinary sperm and the Arctic sperm whale consist of oleyl alcohol, whilst Hilditch and Lovern [44] give the percentage of the alcohol in sperm body oil as 66–70 per cent. and that in the head oil as about 27–30 per cent. of the total higher alcohols present. According to Lovern [41] oleyl alcohol also forms about 30 per cent. of the mixed alcohols present in porpoise head oil.

It is probable, according to Hilditch and Lovern, that small amounts of diethylenic alcohols, $C_{18}H_{34}O$, also occur together with oleyl alcohol in sperm oil.

Oleyl alcohol was prepared synthetically many years ago by the Bouveault-Blanc reduction of ethyl oleate with sodium and amyl alcohol.[35, 51] It is a colourless syrupy liquid which solidifies at about 2° and boils at 208–210°/15 mm., 150–152°/1 mm. The acetate (b.p. 208°/16 mm.) yields nonanoic and acetoxynonanoic acids when oxidised with potassium permanganate, thus establishing the position of the double bond.

Oleyl alcohol is converted into an equilibrium mixture of oleyl and elaidyl alcohols by the action of oxides of nitrogen, but it has not been found possible to separate the geometrical isomerides by crystallisation. Elaidyl alcohol (m.p. 35–35·5°) has, however, been prepared by Toyama [52] by sodium reduction of ethyl elaidate, and also by André and François [53] by a similar procedure. Oleyl alcohol when oxidised by perhydrol in acetic acid yields a 9,10-dihydroxyoctadecyl alcohol (m.p. 82°), whilst elaidyl alcohol gives with the same reagent an isomeric alcohol, m.p. 125–126°; when oleyl or elaidyl hydrogen phthalates are oxidised in dilute alkaline solution with potassium permanganate, the product from oleyl hydrogen phthalate is the hydrogen phthalate of the 9,10-dihydroxyoctadecyl alcohol which melts at 125–126°, and that from elaidyl hydrogen phthalate is the corresponding ester of the isomeric alcohol, m.p. 82°.[54] These relationships are parallel in all respects with those of oleic and elaidic acids when submitted to oxidation by the respective reagents (*cf.* Chapter IX, p. 405).

$\Delta^{9,12}$-**Octadecadienol (Linoleyl alcohol)**, $CH_3.[CH_2]_4.CH{:}CH.CH_2.CH{:}CH.[CH_2]_7.CH_2(OH)$, which may or may not be amongst the small amounts of diethenoid C_{18} alcohols present in sperm whale oils, has been prepared artificially by Turpeinen [55] by Bouveault-Blanc reduction of methyl linoleate. It melts at −5° to −2°, and boils at 148–150°/1 mm.; it furnishes a *p*-nitrophenylurethane, m.p. 91–92°, and unites additively with bromine to give small yields of a tetrabromo-octadecanol, m.p. 87°.

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* It may be mentioned that these plant and insect waxes usually also include, in addition to the wax esters of higher "even-number" normal aliphatic alcohols and acids, hydrocarbons (*n*-paraffins) containing an *odd number* of carbon atoms and including, in different cases, paraffins of the odd-number series from C_{25} to C_{37}.[39] *n*-Nonacosane, $C_{29}H_{60}$, and *n*-hentriacontane, $C_{31}H_{64}$, are frequently major constituents of the hydrocarbon fractions of some of these waxes.

Other natural unsaturated higher aliphatic alcohols. Japanese investigators have reported the occurrence of the following (in each case in minor proportions) :

	ALCOHOL	STRUCTURE	SOURCE	INVESTIGATORS
$C_{10}H_{19}(OH)$	Decenol	Undetermined	Sperm blubber	Ueno and Koyama.[42]
$C_{12}H_{23}(OH)$	Dodecenol	„	„ „	„ „ [42]
$C_{14}H_{27}(OH)$	Δ^{5}-Tetradecenol (physeteryl)	$CH_3.[CH_2]_7.CH:CH.[CH_2]_3.CH_2(OH)$	Sperm head	Toyama and Tsuchiya.[56]
$C_{16}H_{31}(OH)$	Δ^{9}-Hexadecenol (zoomaryl)	$CH_3.[CH_2]_5.CH:CH.[CH_2]_7.CH_2(OH)$	„ „	„ „ [56]
„	„ „	„	Sperm blubber	Toyama and Akiyama.[57]
$C_{20}H_{35}(OH)$	Eicosatetraenol (catadonyl)	Undetermined	„ „	„ „
$C_{22}H_{35}(OH)$	Docosapentaenol (clupanodonyl)	„	„ „	„ „

Hilditch and Lovern[44] estimate that sperm head oil contains about 4 per cent. of hexadecenyl alcohol, and about 10 per cent. of an eicosenyl alcohol, $C_{20}H_{39}(OH)$, smaller amounts of the latter also occurring in sperm blubber oil.

It may also be added here (although it cannot yet be asserted that there is necessarily any connection between the alcohols about to be mentioned and those of the lipid waxes) that Takei *et al.*[58] have detected the presence of the monoethenoid aliphatic alcohols hexenol, $C_6H_{11}(OH)$, and nonenol, $C_9H_{17}(OH)$, in the growing leaves of a number of plants (including tea, ivy, clover, oak, wheat, cypress, and violet).

GLYCEROL ETHERS (CHIMYL, BATYL, AND SELACHYL ALCOHOLS)

These three compounds are found, usually in small quantities, in the non-fatty or unsaponifiable matter left after hydrolysis of various marine animal oils, especially those of the Elasmobranch group. In a few liver oils of Elasmobranch fish the quantity of these substances present forms a relatively large proportion of the total "unsaponifiable" matter. The formulæ, chemical structure, and melting points of the three compounds are as follows:

ALCOHOL	M.P.	FORMULA	STRUCTURE
Chimyl	60·5–61·5°	$C_{19}H_{40}O_3$	$CH_3.[CH_2]_{15}.O.CH_2.CH(OH).CH_2(OH)$
Batyl	70–71°	$C_{21}H_{44}O_3$	$CH_3.[CH_2]_{17}.O.CH_2.CH(OH).CH_2(OH)$
Selachyl	liquid	$C_{21}H_{42}O_3$	$CH_3.[CH_2]_7.CH{:}CH.[CH_2]_8.O.CH_2.CH(OH).CH_2(OH)$

Of the three compounds selachyl alcohol is probably most, and chimyl alcohol least, abundant. Their occurrence was first demonstrated in 1922 by Tsujimoto and Toyama,[59] and the latter worker ascertained that each contained two free hydroxyl groups capable of acetylation. Subsequently (1932) André and Bloch [60] brought forward evidence to show that in the original fish oils these compounds are present in the form of fatty acid esters, each of the free hydroxyl groups being combined with a higher fatty acid.

Although at first there was some uncertainty as to whether the molecular formula of batyl alcohol was $C_{20}H_{42}O_3$ or $C_{21}H_{44}O_3$ Toyama definitely established the latter as being correct in 1924, while at the same time he announced the isolation of the lower saturated homologue, chimyl alcohol, of formula $C_{19}H_{40}O_3$; Tsujimoto and Toyama had previously shown that selachyl alcohol, $C_{21}H_{42}O_3$, passed into batyl alcohol by hydrogenation.

Having shown that dry distillation of selachyl acetate gave rise to oleyl alcohol, and that its oxidation with potassium permanganate yielded nonoic acid, Toyama expressed its constitution as $CH_3.[CH_2]_7.CH{:}CH.[C_{11}H_{21}O](O.CO.CH_3)_2$. The nature of the third oxygen atom had not been defined up to this point, but in 1926 Weidemann [61] stated that the action of hydriodic acid upon batyl alcohol yielded methyl iodide and that the third oxygen atom was therefore apparently present in the form of a methoxyl group. From 1928 onwards a detailed investigation into the structure and synthesis of batyl and chimyl alcohols was carried out by Heilbron and co-workers who, in the first place, repeated Weidemann's experiments and found that the alkyl iodide produced was in fact octadecyl iodide,[62] so that batyl alcohol must be a monoglyceryl ether of octadecyl alcohol, having the structure (i) or (ii).

(i) $C_{18}H_{37}.O.CH_2.CH(OH).CH_2(OH)$.
(ii) $C_{18}H_{37}.O.CH(CH_2OH)_2$.

The next step was to synthesise one or other of these mono-ethers of glycerol. Condensation of octadecyl chloride with sodium allyl oxide, followed by oxidation of the resultant octadecyl allyl ether with perhydrol, led to the production of *a*-octadecylglyceryl ether, and this had the same melting point (70–71°) as pure batyl alcohol.[63] A mixed melting point determination of the two substances showed, however, a small but definite depression, which was emphasised in the case of the respective diphenylurethanes. It must therefore be concluded either that (*a*) batyl alcohol is actually the β-octadecyl glyceryl ether or (*b*) the natural alcohol is an optically active stereoisomeride of the racemic synthetic α-ether. Although Toyama [64] was unable to detect any optical activity in pure batyl alcohol, Knight,[65] from evidence provided by measurements of unimolecular films of batyl, chimyl, and selachyl alcohols, favoured the unsymmetrical α-glyceryl ether structures. That the latter view is correct was finally proved by Davies, Heilbron, and Jones [66] who oxidised batyl alcohol with lead tetra-acetate, a reagent which, as shown by Criegee,[67] is specific for αβ-glycols, and identified formaldehyde and glycollic aldehyde octadecyl ether (m.p. 51°) in the fission products. In view of this, the optical properties of batyl alcohol were again examined, when it was ascertained that, contrary to the finding of Toyama,[64] the alcohol exhibits small but definite optical activity, its specific rotation in chloroform being $[\alpha]_{5461}^{20}$ +2·6° (c., 0·95). The activity is more readily demonstrated in the case of batyl acetate, the specific rotation of which is $[\alpha]_{5461}^{20}$ − 8·5° in chloroform (c., 2·63).

The synthesis of α-cetyl glyceryl ether (m.p. 61–62°) was effected by the same method as that described for the synthesis of the α-octadecyl homologue, and, although no direct comparison with the naturally occurring chimyl alcohol (m.p. 60·5–61·5°) was possible there is little doubt that this also is α-cetyl glyceryl ether.

The synthesis of β-cetyl glyceryl ether (m.p. 61–62°) and β-octadecyl glyceryl ether (m.p. 62–63°) was subsequently achieved by condensing the sodium salt of *αα'*-benzylidene glycerol with cetyl or octadecyl iodide, followed by hydrolysis of the resultant product.[68] Each product gave several degrees depression in melting point when mixed with the natural chimyl or batyl alcohols.

An alternative synthesis of batyl alcohol by Kornblum and Holmes [70] starts from the condensation of *n*-octadecyl iodide with sodium allyl oxide, CH_2:CH.CH_2(ONa), which affords *n*-octadecyl-allyl ether in good yield. The ether, when treated with peracetic acid in acetic acid solution at 80–85°, yields batyl alcohol, m.p. 70–71°.

As the batyl alcohol employed by Davies, Heilbron, and Jones (above) was prepared from selachyl alcohol it follows that the latter must be α-oleyl glycerol ether.

The synthesis of the optically active forms of chimyl and batyl alcohols from *d*- and *l*-acetonyl glycerols and the corresponding alkyl iodides by Baer and Fischer [34d] has already been mentioned earlier in this chapter (p. 454).

The occurrence of these glyceryl ethers in nature is a matter of considerable biological interest. The pure alcohols have neither growth-promoting nor antirachitic properties (Weidemann [61]) and their function, if any, in the animal organism is at present obscure. From the standpoint of chemical structure, they represent in some measure an intermediate link between glycerides (true fats) and waxes as shown below.

GLYCERIDE	GLYCERYL ETHERS	WAXES
$(R.CO.O)_3.C_3H_5$	$(R.CO.O)_2.C_3H_5(OR')$	$R.CO.O.R'$

$(R = CH_3.[CH_2]_7.CH{:}CH.[CH_2]_7—$, $CH_3.[CH_2]_{16}—$, or $CH_3.[CH_2]_{14}—$;
$R' = CH_3.[CH_2]_7.CH{:}CH.[CH_2]_8—$, $CH_3.[CH_2]_{17}—$, or $CH_3.[CH_2]_{15}—)$

Lovern [69] has indeed suggested that, since appearance of these alcohol-ethers in fish oils is invariably accompanied by sub-normal unsaturation in the fatty acids of the oil, their production may be regarded as evidence of an unusual tendency towards saturation or hydrogenation in the fish oils in question ; so that the alcohol-ethers represent a hydrogenation of the glyceride molecule which has involved the reduction of an ester-carbonyl group. This is well illustrated by the liver oil of the ratfish,[69] which contains nearly 37 per cent. of these compounds (mainly selachyl, with a little chimyl and batyl, alcohol), the fatty acids of the oil including 50 per cent. C_{18} unsaturated (mean unsaturation only —2·2H), 20 per cent. C_{20} unsaturated (mean unsaturation only —2·9H) and 8 per cent. C_{22} unsaturated (mean unsaturation only —3·5H). Incidentally it may be noted that ratfish liver oil consists substantially of di-acyl esters of selachyl and the related alcohol-ethers, with practically no glycerides.

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CHAPTER XI

NOTES ON EXPERIMENTAL TECHNIQUE EMPLOYED IN THE QUANTITATIVE INVESTIGATION OF FATS

IT seems desirable to conclude this book by a description of the experimental methods which have so far found acceptance in the quantitative or semi-quantitative study of the natural fats. A fairly full account of some of the experimental technique is included, although in other instances the treatment is more general. In particular, the more or less standard methods for the determination of characteristics such as iodine and saponification values are not here given in detail. Workers in this field will be, for the most part, already familiar with the procedure to be followed in determinations of the latter kind; in any case, full details are available in monographs on these more usual forms of fat analysis, such as the well-known works of Lewkowitsch [1] or Grün,[2] or the more recent volumes of Bolton,[3] Elsdon,[4] or Dean.[5]

It may be pointed out here that the determinations ultimately required in quantitative study of component acids or glycerides of natural fats are, almost wholly, those of mean molecular or equivalent size, and of mean unsaturation. The determination of the former (i.e. saponification value or saponification equivalent, the latter form being on the whole more useful in work of this kind) is a standard operation of fat analysis; it need only be added that, since much depends on the accuracy of each determined equivalent in the subsequent calculations, extreme care should be taken to maintain the greatest possible exactitude in all determinations of saponification equivalents. Mean unsaturation is usually evaluated by iodine values, determined preferably by the Wijs or Hanus methods. Special cases may however arise here. Thus, in mixtures of oleic, linoleic, and linolenic compounds it may be desirable to determine each separately, either by alkali isomerisation followed by spectrographic analysis, or thiocyanometrically (*cf.* p. 138). Also, if conjugated unsaturation is present, determination of the total unsaturation by the Wijs or Hanus procedures is not possible.

The procedures with which we are about to deal fall into two separate categories, those employed in determining the proportions of the components in the mixture of *fatty acids* present in a natural fat, and those used in the estimation of the chief component *glycerides* of a natural fat.

NOTES ON EXPERIMENTAL TECHNIQUE

I. Quantitative Investigation of Component Fatty Acids

A mixture of higher fatty acids such as is usually present in natural fats is ultimately resolved, by fractional distillation in a vacuum of the corresponding methyl (or ethyl) esters, into a series of ester-fractions which contain substantially not more than two saturated, and not more than two homologous groups of unsaturated, esters. It is rarely advisable, however, to convert the mixture of fatty acids as a whole into methyl (or ethyl) esters and then to attempt to separate the latter by fractionation. Usually it is very much better to apply certain preliminary separations which, although not always complete as regards the individual acids, lead to the subsequent production of two or three groups of esters, the subsequent treatment of each of which is considerably simplified by comparison with that of the esters of the whole of the original fatty acids.

In the majority of cases (when acids of lower molecular weight than octanoic, $C_8H_{16}O_2$, are absent) the only preliminary separation needful is to segregate, as far as possible, the saturated from the unsaturated members. This has almost always been effected until recently by taking advantage of the differing solubility in alcohol of the lead salts of these two types of fatty acids; but an alternative method is now available, namely, fractional crystallisation of the mixed acids from appropriate solvents over a range of temperatures down to —50° C. or lower.

When, however, the fats contain appreciable amounts of acids of lower molecular weight than octanoic (caprylic), it is necessary to remove the more volatile acids of lowest molecular weight before proceeding to separate the higher saturated and unsaturated acids. This only applies in the cases of the acids of milk fats, dolphin, and porpoise oils and a few others, but for the sake of completeness it is preferable to deal with this contingency before discussing the more general separation procedures.

Preparation of the mixed fatty acids from a fat. The quantity of fatty acids requisite for an accurate analysis depends upon the complexity of the mixture of component acids. Where this is very simple (for instance, in some of the Lauraceæ seed fats, etc.), a reasonably accurate determination may be made with as little as 20 grams of fat. In many of the more common vegetable fats, in which there are perhaps only three or four major component acids but, in addition, small proportions of other minor component acids, it is desirable to work with 70–100 g. of fat in order to take due account of the proportions of the minor components. In other cases (for example, pig and ox depot fats), especially where close accuracy is desired in the percentages of several minor component acids, it is advantageous to commence from 150–200 g. of fat, whilst for fats with very complex mixtures of component acids, such as fish oils and milk fats, from 200 g. to 500 g. of fat may be required in order to obtain the final production of sufficient ester-fractions of the necessary degree of simplicity referred to above.

It is clearly desirable that complete hydrolysis of the original fat be ensured, and therefore it is well, in most cases, to saponify 100 parts by weight of fat with a solution of 30 parts by weight of potassium hydroxide in about 500 parts of alcohol (95–100 per cent.); the solution is boiled freely under reflux condenser for 3 hours, and most of the alcohol then removed by distillation. The soaps are dissolved in water and, after removal where necessary of unsaponifiable matter (*vide infra*), converted into the free fatty acids by warming with dilute sulphuric acid.* When the acids are completely liberated, they may be removed by extraction with ether and are eventually dried under vacuum at 100°.†

When highly unsaturated acids are known to be present in quantity, as in fish and some other oils, it is not desirable to employ any large excess of alkali or to prolong the saponification process unduly, because of the readiness of such acids to undergo isomeric rearrangement under these conditions. It then becomes preferable to risk the chance of slightly incomplete conversion of the whole fat into fatty acids rather than to incur rearrangement of some of the highly unsaturated components, and in these cases the use of only a slight excess of alkali over that theoretically required, with heating under reflux for only one to two hours, is advised.

Removal of unsaponifiable matter from the mixed fatty acids. Normally speaking, all the unsaponifiable matter present in a fat tends to pass with the alcohol-soluble lead salts, or with the most soluble fraction of low-temperature solvent-crystallised acids, into the esters of the "liquid" or mainly unsaturated acids (*vide infra*), and finally to appear in the small residue of these esters left undistilled. In certain circumstances, unsaponifiable or non-fatty matter may be present which distils at about the same temperature as one or more of the methyl esters and therefore accompanies the latter in some of the ester-fractions. In such cases it is very desirable to remove unsaponifiable matter before the acids are converted into esters; whilst if its amount exceeds 1 or 2 per cent. of the whole fat, its presence in the above-mentioned residual ester-fraction makes accurate analysis of the latter very difficult. Frequently, therefore, but not necessarily with fats (such as tallows, etc.) in which the amount of unsaponifiable matter is 0·5 per cent. or less, it is best to remove as much unsaponifiable matter as possible by extracting with ether the aqueous-alcoholic solution of the soaps (before converting these into the free fatty acids).

To avoid the cumbersome and not too efficient extraction of large volumes of soap solution with ether in separating funnels, a continuous extractor such as that shown in Fig. 5 may usefully be employed. The soaps are largely diluted with water until they occupy about two-thirds of the large bottle B, about 200 c.c. of alcohol being also added to retard emulsification. The remainder of the bottle is filled with ether, whilst the litre flask A is about half filled with ether, which is boiled, the vapours passing through the condenser C. The condensed ether passes into a long tube leading nearly to the bottom of B, where it is preferably dispersed by a small glass stirrer [6] rotated by a motor at a speed regulated so that minimum formation of emulsions sets in. The stirrer shaft passes through the cork of the bottle in glass tubing which is continued to about 9 inches below the level of the ether return tube; the long delivery tube is widened at the top so as to surround the exit tube from the condenser. Well-rolled good quality corks are suitable for attaching the various tubes to the flask A, the bottle B, and the condenser C.

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* When unsaturated acids are present in quantity, it is advisable to liberate the free acids under an atmosphere of carbon dioxide.

† See, however, the special case of mixed fatty acids in which volatile acids of low molecular weight are present (p. 467).

As the ether condenses into B, the supernatant layer of ether in the bottle is displaced back into the flask A by the hydrostatic pressure set up in the long delivery tube, and the extraction process is continuous. This apparatus gives less trouble with emulsions than the use of separating funnels, and about 95 per cent. of the unsaponifiable matter is removed from the solution in the course of 24 hours' extraction. At the end of the operation the ether in A and that in the upper part of B are united and washed with dilute alkali solution and then with water to remove any soap; the aqueous alkali solutions are mixed with the main extracted soap solution, from which the fatty acids are liberated as described above.

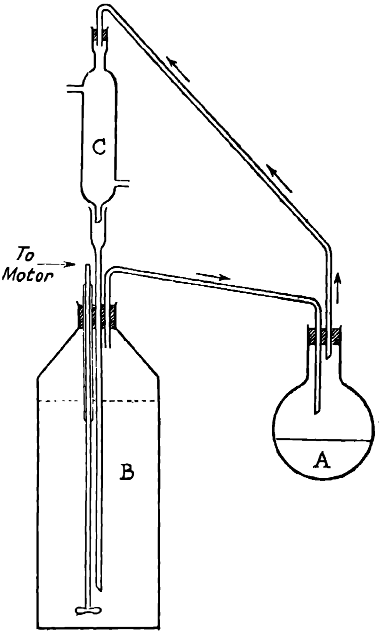

FIG. 5.

PRELIMINARY SEPARATIONS OF THE MIXED FATTY ACIDS

(a) Separation of volatile from non-volatile acids

In the case of the acids of milk fats and a few other fats which contain butyric, *iso*valeric, or hexanoic acids, the latter may first be removed from the mixed fatty acids by distillation in a current of steam. A convenient procedure is as follows:

After hydrolysis of the fat with alcoholic * alkali, it is essential to remove alcohol completely from the soaps before acidifying, owing to the readiness with which butyric acid esterifies. After distilling off as much alcohol as possible, the remaining traces are removed by heating the soaps in a steam bath under the vacuum of a water pump, water being added, when necessary, to keep the soaps in solution as far as possible. The fatty acids are liberated from the soaps by the addition of 10 per cent. excess of sulphuric acid (40 per cent. solution), the acid being preferably added to the cold soap solution, and the mixture being cooled to prevent loss of butyric acid by volatilisation. Steam distillation is then commenced, using a double spray trap, and after about half an hour, the soaps become completely decomposed, giving a clear layer of fatty acids floating on the surface of the aqueous solution. Distillation is continued for four or five hours, in order to remove all the butyric and hexanoic acids. Small quantities of octanoic and decanoic acids also pass over into the steam distillate, together with traces of oleic and/or decenoic acid.

The fatty acids in the steam distillate are extracted by means of pure ether and are fractionated directly from a plain Willstätter bulb (*cf.* p. 476), mainly at atmospheric pressure; the residue from the fractionation is tested for iodine value as well as equivalent, and the iodine value calculated to oleic (or, if preferred, to decenoic) acid. The extracted aqueous liquors and the recovered distilled ether must both be titrated with alkali, the small amounts of acid being calculated as butyric acid. The full details of a typical fractionation analysis of a butter fat are given in Table 105 in order to illustrate the application of this method.

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* The alcohol used in the saponification must first be thoroughly refluxed with caustic soda and then distilled from the caustic alkali, in order to remove any traces of aldehyde, acetic or other lower acids, the presence of which would interfere with the determination of the volatile acids from the fat.

The residual, non-steam-volatile fatty acids, after cooling in an atmosphere of carbon dioxide to prevent oxidation, are extracted with ether, the ether solution is washed free from mineral acid, the ether removed by distillation and the acids finally dried by heating at 100° for a short time in the vacuum of a water pump. They are then submitted to a lead salt separation (*cf.* (*b*) below) in the usual way.

(*b*) **Separation of saturated from unsaturated acids by lead salts**

The separation of " solid " (or mainly saturated) from " liquid " (or mainly unsaturated) higher fatty acids by extraction of their mixed lead salts with ether was introduced by Gusserow[7] in 1828 and improved by Varrentrapp[8] in 1840. This process (details of which have been given by Lewkowitsch[9]) involves preliminary precipitation of the lead soaps from the aqueous alkali soap solutions and subsequent extraction of the washed precipitated lead soaps with ether. It has been largely superseded * by separation of the lead salts from alcohol, instead of ether, solutions, an improvement which was first suggested by Twitchell.[10]

Twitchell recommends adding, to a solution of mixed fatty acids containing 1–1·5 g. of saturated acids dissolved in boiling 95 per cent. alcohol (30 c.c.), a solution of lead acetate (about 1·5 g.) in boiling 95 per cent. alcohol (70 c.c.), cooling the mixed solutions slowly to 15° C., and leaving them overnight; the separated lead salts are filtered off, washed with 95 per cent. alcohol until, on dilution, the washings remain clear, and are then recrystallised from 95 per cent. alcohol (100 c.c. containing 0·5 g. glacial acetic acid). The cooling process is repeated, and eventually the separated, washed lead salts are converted by acidification with nitric acid into the free acids, in which form they are weighed.

The proportion of alcohol employed in the first precipitation per unit weight of mixed fatty acids may thus vary, according to the expected percentage of saturated acids in the latter, from about 10 to 30; for mixed fatty acids containing about 30 per cent. of saturated acids it is about 20. Again, whilst Twitchell mentioned the use of sufficient lead acetate to interact with all the fatty acids present, he was inclined to recommend that the lead acetate should be taken so as to be only somewhat in excess of that required for combination with the saturated acids; later workers have reverted to some extent to the use of larger proportions of lead acetate, and in the application of the Twitchell method to directly saponified fats Baughman and Jamieson[12] advocate the employment of 5 g. of lead acetate per 1–1·5 g. of solid acids present in the original fat. Cocks, Christian, and Harding[13] have shown that the Twitchell process can be applied to mixtures of fatty acids containing *iso*oleic acids of hydrogenation, with an accuracy of about ±2 units per cent., by employing a larger proportion of lead acetate to fatty acids and by recrystallising the initially separated lead salts from petroleum ether instead of from a further quantity of 95 per cent. alcohol (for details, *cf.* original paper[13]).

The processes just mentioned are designed chiefly for use in the analysis of small quantities of fatty acids. For the separation of the larger amounts of acids involved in determination of component acids by ester fractionation, it has been found convenient to introduce some further modifications into the Twitchell method. In the writer's laboratory at Liverpool, the usual procedure is as follows:

The mixed fatty acids (e.g. 200 g.) are dissolved in 95 per cent. alcohol (1,000 c.c.), the solution is boiled and mixed with a boiling solution of lead acetate (140 g.) in 95 per cent. alcohol (1,000 c.c.) (the alcohol in both cases containing 1·5 per cent. of glacial acid).[*] The lead salts which are deposited on cooling at 15° overnight are recrystallised from a volume of alcohol, also containing 1·5 per cent. of glacial acetic acid, equal to that used in the first instance, the " solid " acids are regenerated from the recrystallised lead salts, and the " liquid " acids recovered from the lead salts left on evaporation of the mixed alcoholic filtrates from both operations.[†] Each group of acids is converted into neutral methyl esters by boiling with four times its weight of methyl alcohol in presence of about 1 per cent. of concentrated sulphuric acid, and (after distilling off about 70–80 per cent. of the methyl alcohol) taking up in ether and removing unesterified acid by washing with dilute potassium carbonate solution. The conversion into methyl esters is usually 97–98 per cent.

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* For a bibliography of the many modifications proposed in connection with the Gusserow-Varrentrapp process, see Bertram.[11]

Unless due precautions are observed, acids of the more unsaturated types (e.g. from " drying " oils such as linseed and especially tung oil and their analogues, or from aquatic fats) are liable to undergo polymeric or other changes during the esterfication. This has been shown to be especially likely to occur during concentration of the mineral acid by removal of the methyl alcohol. In such instances, therefore, it is essential (*a*) to employ the minimum concentration of sulphuric acid to secure nearly complete esterification (probably as little as 0·5 per cent. may suffice), and (*b*) not to remove unchanged methyl alcohol by distillation, but to pour the reaction mixture into cold water and proceed at once to extract the esters from the diluted alcohol with ether. The latter precaution is very important.

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[*] It has been found that the presence of acetic acid leads to much more complete removal of oleic acid from the " solid " acids, although slightly more palmitic and myristic acids also pass into the " liquid " acids (Dr. A. Banks).

[†] Convenient methods of recovering the fatty acids from the insoluble and soluble lead salts are as follows :

The *insoluble lead salts* are transferred to a large porcelain basin with successive quantities of concentrated hydrochloric acid and boiling water. Hydrochloric acid (50 per cent.) is then added to the contents of the basin and the whole warmed until there is a clear layer of fatty acids floating on the aqueous solution (which must be acid to Congo red). After allowing the contents of the basin to cool, the layer of " solid " acids is transferred to a separating funnel, and the aqueous layer decanted into another separating funnel from the solid lead chloride, which is then extracted twice with ether. The ethereal solution so obtained from the extraction of the aqueous solution is run into the funnel containing the "solid" acids. The aqueous solution and lead chloride are extracted with a further quantity of ether and then rejected. The flask used in the crystallisation and the Büchner funnel are washed out into the separating funnel containing the " solid " acids with small quantities of ether and, after the " solid " acids are completely dissolved in ether, warm water being cautiously added if necessary, the ethereal solution is washed free from mineral acid and lead chloride, the washings being re-extracted in the second funnel. The ether is then distilled from the combined ethereal extracts and the " solid " acids freed from traces of ether and water by heating at 100° under reduced pressure.

The *soluble lead salts*, after removal of the solvent alcohol by distillation, are dissolved in ether and washed three times with water : the acetic acid present decomposes the lead salts and the lead acetate so formed is readily soluble in the aqueous layer, which is re-extracted with a further quantity of ether. In order to ensure that the lead salts have been completely decomposed, the ethereal solution is washed with dilute hydrochloric acid and then with water until free from mineral acid. The ethereal extracts of the " liquid " acids are combined, the ether distilled off and traces of ether and water removed by heating in a steam bath under reduced pressure.

In working with large quantities of fatty acids, it is considered inadvisable to use dilute nitric acid for decomposition of the lead salts owing to risk of oxidation of unsaturated fatty acids.

The " liquid " fatty acids obtained in a component acid analysis should be converted into methyl esters, and their fractional distillation carried through with as little delay as possible, in order to minimise alteration by atmospheric oxidation. For the same reason, the unsaturated fatty acids and esters or ester-fractions should always be stored in an atmosphere of nitrogen, preferably in a refrigerator.

The " solid " acids obtained in separations carried out as above contain the whole of any stearic or higher saturated acids present, nearly all the palmitic acid, a considerable proportion of any myristic acid present, and smaller proportions of any lower saturated acids. They will also include, of unsaturated acids, minor percentages of oleic acid with some more definite proportion of mono-ethenoid acids of the C_{20} or C_{22} series, when the latter are present. Mono-ethenoid acids of the C_{16} or lower series, and polyethenoid acids of any carbon content (with the exception of elæostearic and, probably, licanic) will, on the other hand, pass practically wholly into the " liquid " acid group. On the other hand, *iso*-acids from C_{18} upwards of hydrogenated fats, whether of the mono- or poly-ethenoid type, usually give lead salts sparingly soluble in alcohol, so that these pass to a considerable extent into the " solid " acids.

In certain instances, notably unsaturated seed fats, which only contain unsaturated acids of the C_{18} series, and also contain only low proportions (10 per cent. or less) of saturated acids, the proportion of palmitic and any lower saturated acid is preferably determined from fractional distillation of the hydrogenated methyl esters of the total fatty acids. This modified procedure is illustrated in the case of rubber seed oil (Table 109, p. 502).

The " liquid " acids may include, in addition to nearly all the oleic acid present, practically the whole of the more unsaturated acids of the C_{18} or higher series, and the mono-ethenoid acids of the C_{16} or lower series, a certain amount of the *iso*-acids mentioned and of mono-ethenoid acids of the C_{20} or C_{22} series, together with much of the octanoic, decanoic, and lauric acids (when these are present), minor amounts of myristic and traces of palmitic acid.*

Naturally all or most of the acids mentioned in the preceding paragraphs are not frequently encountered in one and the same fat. In actual practice use of the lead salt process in most cases provides a good separation into two groups of fatty acids, each of which is a comparatively simple mixture which is then readily amenable to the ester-fractionation procedure.

When, as in coconut and similar fats, there is a very high proportion of saturated acids of only medium molecular weight coupled with a low percentage of unsaturated acids, it may be preferred to esterify the whole of the mixed fatty acids and to separate all the lower saturated esters (up to those of C_{14} or C_{16} acids) by fractional distillation, and then to hydrolyse the residual esters and apply the lead salt separation only to the remaining mixture of higher fatty acids ; the " solid " and " liquid " acids so obtained will then, of course, be re-esterified and further separated by fractionation in vacuum. On the other hand, it is simpler, in such cases, to determine the linoleic and oleic acid content of the total fatty acids by the spectrographic method[28] (referred to later, p. 473), thereby obtaining the mean unsaturation of the unsaturated C_{18} esters present; with this, a complete fractional distillation of the whole of the mixed esters then gives sufficient data for the calculation of all the acids present.

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* In fats of very high stearic acid content (40 per cent. or more) traces of stearic acid may also appear in the " liquid " acids.

(c) Separation of polyethenoid acids by lithium salts

The mixed fatty acids of whale, fish, or other fatty oils which contain fairly large proportions of polyethenoid acids of the C_{20} or C_{22} series are conveniently submitted, before proceeding to the lead-salt separation, to crystallisation of their lithium salts from 95 per cent. acetone, in which the salts of the highly unsaturated acids are soluble, as first observed by Tsujimoto.[14] The inclusion of this procedure in the ester-fractionation analysis of mixed fatty acids of this nature was worked out by Terleski in the writer's laboratory and described, in the case of whale oil (*cf.* Table 108, p. 498), by Hilditch and Maddison.[15a]

Details of the procedure are as follows[15b]: The mixed fatty acids of the fat are dissolved in acetone (4 c.c. per gm. acids), and the hot solution titrated (to phenolphthalein) with saturated (ca. 4*N*) aqueous lithium hydroxide solution. The solution is then adjusted so that the solvent consists of 95 per cent. acetone,* refluxed for a few minutes, and set aside to cool for two hours at room temperature. The insoluble lithium salts are collected in a Buchner funnel and washed with a small amount of 95 per cent. acetone. Most of the acetone is removed by distillation from the filtrate, which is then transferred to a separating funnel, decomposed by excess of hydrochloric acid, and the liberated, unsaturated acids recovered by extraction with ether.

The insoluble lithium salts are similarly reconverted into fatty acids, to which the usual lead-salt separation may then be applied.

The whale oil acids quoted in Table 108 thus yielded 16·8 per cent. of acids (iodine value 307·5) as soluble lithum salts, subsequent lead-salt separation of the remainder giving 58·8 per cent. (iodine value 105·1) of acids from soluble lead salts, with 23·5 per cent. (iodine value 10·7) of acids from the insoluble lead salts.

(d) Separation of mixed fatty acids by crystallisation from solvents at low temperatures

It was mentioned in Chapter IX (pp. 398, 420) that individual unsaturated acids can be isolated in considerable purity by crystallisation from appropriate organic solvents at low temperatures (down to −70° C.), this technique having been developed especially by J. B. Brown and his colleagues. In a comprehensive review on the low-temperature crystallisation of fatty acids Brown[16a] has stated that, for analytical purposes (including separations precedent to fractionation of the fatty acid esters), the crystallisation procedures are preferable to chemical (lead salt, etc.) methods of resolution by reason of their simplicity and directness. The present writer supports this unreservedly in those instances in which the acids of a fat are largely unsaturated, and especially if they are mainly polyethenoid; here the conversion of such acids into salts, and the subsequent reconversion of the latter to the free acids, offers opportunities for changes (either of oxidation by exposure to air, or in some cases isomeric rearrangement) which are best avoided. On the other hand, the lead-salt separation is not open to these objections in many fats, e.g. animal body fats and not a few solid vegetable fats, and, being equally simple in operation and not requiring the

* The volume of pure acetone to be added approximates to [19×10/11×c.c. of LiOH solution used−100] c.c.

special devices necessary for the production and maintenance of low temperatures, it may well continue to be widely used in many instances.

In the writer's experience, stearic and palmitic acids are usually more completely and effectively removed by lead salt separation than by the crystallisation procedures, this being another, if minor, advantage in favour of the former. On the other hand, in the many vegetable and marine animal fats in which the proportion of saturated acids is low (often not more than 10 per cent. of the total acids), their removal by lead-salt separation is in any case far from complete, and in such cases it now seems far better to replace preliminary separation by lead salts by preliminary low-temperature crystallisation.

Foreman and Brown [16b] have given a comprehensive survey of the solubilities of the saturated acids from lauric to behenic, and of oleic, linoleic, linolenic, eicosenoic, and erucic acids, in acetone, methyl alcohol, and petroleum (b.p. 57–63°) at temperatures down to —50° C. and lower. In this report they point out two factors which are of great importance in the practical application of this technique :

(*a*) Cooled solutions of fatty acids come to equilibrium exceedingly slowly at low temperatures, and it is therefore desirable to afford as long as possible for the crystallisation.

(*b*) Although the higher saturated acids are only very slightly soluble in many of the pure solvents (e.g. palmitic acid in acetone at —30°, 0·38 gm. per litre, in ether at —40°, less than 0·1 gm. per litre), the presence of other acids (e.g. oleic or linoleic) of greater solubility introduces mutual solubility effects which may cause the retention in solution of considerably more of the saturated acid than would be expected from the data for pure solvents.

It will be inferred, therefore, that the low-temperature crystallisation procedure has much in its favour as a means of preliminary resolution of mixed fatty acids, and that each case must be considered, in selecting the solvent and the most suitable temperatures of separation, in relation to the particular mixture of acids present in the fat under examination. General indications only will be offered here.

The method was probably first employed in a component fatty acid analysis by Cramer and Brown [16c] in the case of human depot fats, when distilled methyl ester fractions of the mixed fatty acids, corresponding respectively to the C_{14}, C_{16}, and C_{18} acid series, were further resolved by crystallisation from methyl alcohol, petrol, or acetone, at temperatures from —20° to 70° C. De la Mare and Shorland [17] crystallised the mixed methyl esters of a pig back fat from acetone (15 c.c. per gm. esters) three times at —35° C. prior to ester fractionation of the insoluble and combined soluble esters.

Hilditch and Riley [18a] studied the crystallisation procedure as applied to sunflower seed, sesame, and groundnut oils, in all of which oleic and linoleic acids together form 80 per cent. or more of the total fatty acids. Crystallisation of the mixed acids was on the whole preferred to that of their methyl esters, and good results were obtained by first crystallising the mixed acids from acetone (5 c.c. per gm.) at —30° C. (when most of the linoleic acid was left in solution), followed by crystallisation of the solids (separated from acetone at —30° C.) from ether (10 c.c. per gm.) at —30° C., the least soluble portion so obtained having a comparatively low iodine value (10–20).

Gunstone and Hilditch [18b] applied the method to linseed and rubber seed oils. Here it was found that crystallisation from acetone (5 c.c. per gm.) at —50° C. yielded a filtrate with most of the linolenic acid and but little oleic acid, whilst further crystallisation of the solids deposited at —50° C. from acetone at —30° C. gave a filtrate in which linoleic and/or linolenic acid was the major component, with subordinate proportions of oleic (and sometimes linolenic) acids. The solids deposited from acetone at —30° C. were finally crystallised from ether (10 c.c. per gm.) at —30° C. and deposited solid acids of low iodine value, leaving in solution a mixture of unsaturated acids with, however, minor proportions of palmitic and stearic acids. The latter acids were also present in very small amounts in the filtrates from acetone at —50° and —30° C. The proportions of the three unsaturated acids in each group of mixed acids obtained by crystallisation were determined spectrographically after alkali isomerisation (*cf.* Chapter IV, pp. 138, 154). It may be mentioned that in the initial crystallisation from acetone it was found best, for ease of removal of the deposited acids, to cool first at —30° C., filter, then cool the filtrates to —50° C. The crystals deposited at —30° and at —50° C. were then united and recrystallised from acetone at —30° C.

Hilditch and Riley [18c] modified the method further to meet the case of fatty oils in which the conjugated elæostearic acid is present in quantity. Here the preferred mode of crystallisation is (after removal of unsaponifiable matter from the aqueous solution of soaps from the saponified fat) to crystallise the mixed fatty acids first from acetone (5 c.c. per gm.) at —30°. The separated acids were then recrystallised from acetone (10 c.c. per gm.) at —60°, when solid acids were deposited which included much of the elæostearic acid and most of the saturated acids present. The acids left in solution in both acetone crystallisations were united and crystallised from petrol (b.p. 40–60°, 10 c.c. per gm.) at —60°, when a concentrate of linoleic and other unsaturated acids with 15 per cent. or less of elæostearic acid was left in solution ; the acids deposited at —60° were finally recrystallised from the petrol (10 c.c. per gm.) at —40°, giving a solid fraction rich in elæostearic acid and a soluble portion similar to that left in solution at —60°, but containing more oleic and, usually, less linoleic acid.

The elæostearic acid content of all four groups of acids was determined by direct spectrographic measurement of the intensity of the absorption band at 268 mμ. Alkali-isomerisations at 170° and 180° then gave the data for linolenic and linoleic acids as in the case of the linolenic acid-containing oils discussed above. Owing to the uncertainty of iodine value determinations in the case of elæostearic acid, the oleic acid is not, in this group, determined by difference from the total iodine value of the acids present. Instead, the combined amount of oleic+saturated acids is arrived at by difference, and the content of saturated acids is determined on a separate sample of the total mixed acids of the original fatty oil by the Bertram oxidation method.

Finally, in unsaturated fatty oils with low proportions of saturated acids it has been found advantageous not to determine individual saturated acids by ester-fractionation of each group of acids separated by low-temperature recrystallisation. Instead, a separate quantity (70–80 gm.) of the total mixed fatty acids of the oil is converted into methyl esters, which are hydrogenated at 100–110° C. in presence of Raney nickel catalyst to almost complete saturation. The hydrogenated esters are then fractionally distilled and the content of palmitic (and, if present, myristic) ester determined in the usual way from the saponification equivalents of the lower boiling fractions. The proportion of stearic (+arachidic, etc.) acid in the original oil is then obtained by difference from the total saturated acid content as given by the Bertram oxidation procedure.

Illustrative details of the method as applied to Ceylon rubber seed oil are given in Table 109 (p. 502). The degree of accordance between component acid analyses for groundnut, sunflower seed, and sesame oils, carried out by the crystallisation procedure and also by preliminary lead-salt separation, is shown in Table 110C (p. 512).

As already stated, conditions must be chosen to some extent to suit the individual case, but the following general points may be mentioned. The solution to be cooled is placed in a beaker or, perhaps preferably, a round-bottomed flask, immersed in a bath containing alcohol, this bath being surrounded by several inches of sawdust or other non-conducting material in a wooden or stout cardboard box. The alcohol bath is cooled to the desired temperature by the addition of solid carbon dioxide.

It seems desirable to cool slowly at first until a nucleus of crystals has separated, after which cooling can be rapidly effected ; this aids in the formation of a deposit of crystals which filter readily. If desired, mechanical stirring may be maintained throughout, but it is perhaps simpler, and almost as efficacious, to rely on intermittent stirring by a rod manipulated by hand.

It is important, for reasons already stated, to allow the mixture to remain for as long as possible at the crystallisation temperature. At least 4–5 hours should be given, whilst even more would be an advantage.

The solution may eventually be filtered either by insertion of a cooled sintered-glass filter plate fused to a glass delivery tube, or by transference to a Buchner funnel enclosed in a wooden box, the space between funnel and box being packed with crushed solid carbon dioxide so that the funnel temperature is the same as that to which the solution has been cooled.

In the case of the more unsaturated fatty oils, a further advantage of the crystallisation procedure is that the most unsaturated (and soluble) acids, separated from the initial crystallisation at the lowest temperature of the series, can immediately be esterified and fractionated, etc., thus securing that the acids most prone to oxidation are handled with minimal time for exposure to air and possible alteration.

FRACTIONAL DISTILLATION IN A VACUUM OF HIGHER FATTY ACID ESTERS

As already stated (p. 469), those portions of the mixed fatty acids which are to be further resolved by ester-fractionation are converted into methyl esters by boiling with about four times their weight of methyl alcohol in presence of about 1 per cent. of concentrated sulphuric acid, and subsequently removing unesterified acid by washing the ether solution of the esters with dilute potassium carbonate solution. The conversion into methyl esters is usually 97–98 per cent., but if by accident it falls below this figure, the unesterified acid should be recovered and re-esterified.

It has become the custom to use methyl esters, primarily because of their slightly lower boiling points as compared with those of ethyl esters. With the vacua (0·1–0·2 mm.) now readily obtainable with the ordinary rotary oil pumps, this point is of less significance than formerly, but it is convenient to continue with the (methyl) esters with which so much data have already been obtained, owing to the possible confusion in calculation of results which might ensue from the use, in different cases, of methyl and of ethyl esters. However, in the special case of saturated acids higher than stearic, the use of ethyl esters has the minor advantage that their melting points are definitely lower than those of the corresponding methyl esters, so that less difficulty may be caused during their distillation by premature solidification in the receiver.

The vacuum employed should *not be extreme*; for example, that (0·00001 mm.) obtainable by a mercury or oil diffusion pump would have the effect of lowering the boiling points of the component esters so far that the temperature gap between the boiling point of one member and the next higher in the series would become unnecessarily small. Fractional distillation of higher fatty esters was quite feasible with the vacua of 3–5 mm. provided by the rotary oil pumps available 15–20 years ago, and is a matter of great ease with the present-day rotary oil pumps which readily give a working vacuum of 0·1–0·2 mm. At these low pressures, as is well known, it is not easy to determine the precise pressure at the head of the column of distilling vapour, and moreover the latter may vary slightly during a distillation owing to the inconstancy of minute leaks in the cork and rubber connections on the apparatus. Consequently the recorded boiling points at the head of the fractionating column have little or no absolute significance in this kind of work. On the other hand, the column head temperatures should be systematically recorded, since in conjunction with those of the heating bath (and in some cases, of the centre of the fractionating column) they afford a reliable indication of the smooth running, and therefore of the efficiency, of the fractionation.

As a rough approximation, it may be added that, at about 0·2 mm. pressure, the column head temperatures for methyl laurate, methyl palmitate, and methyl oleate (or stearate) are usually respectively about 75–80°, 110–115°, and 130–135° C.

Distillation from a simple form of fractionating flask. Unless small proportions of minor component esters are required to be determined, fractional distillation of the esters from a simple distilling flask of the "Willstätter" pattern (shown with receiver in Fig. 6) is sufficient to resolve most of the ester mixtures which are usually encountered, providing that where necessary one or more of the fractions from the primary distillation are refractionated. This simple type of apparatus was in constant use in the determination of component fatty acids in the writer's laboratory at the University of Liverpool for many years. A more efficient electrically heated column (*cf.* p. 479) was adopted subsequently, primarily to aid in the study of ester mixtures which included small amounts of myristic, palmitic, and hexadecenoic esters, or complex mixtures of esters such as those of the "solid" or the "liquid" acids of milk fats. It has been found convenient generally to employ this more elaborate column for nearly all ester-fractionations, but for the less complex and more easily separable ester mixtures the simpler "Willstätter flask" apparatus is entirely adequate. The figures given in Table 106 (pp. 491–493) illustrate the accordance in results obtained with each form of distillation apparatus in the case of the "liquid" (mainly unsaturated) esters of a pig back fat.

It may be pointed out, however, that, although the time taken for a distillation through the electrically heated column may be considerably longer than with the Willstätter flask, refractionations of primary fractions are avoided, so that often the former may economise also in the overall time consumed in an analysis.

The dimensions of the bulb are important, in order to achieve maximum efficiency. The lowest bulb, containing the esters to be distilled, should not be less than 8 cm. diameter (250 c.c. capacity). A smaller bulb should not be employed, even for small batches of esters; the 250 c.c. bulb will take a load of up to 150 g. of esters. For larger quantities a 500 c.c. bulb (ester capacity 300 g.) may be substituted.

The intermediate bulb should be 5·2 cm. in diameter, and the upper one 4·4 cm. in diameter; the diameter of the cylindrical portions of the neck should be 3·2 cm. throughout (all measurements refer to internal diameters). The height from the neck of the flask to the top of the lowest bulb should be 22 cm.

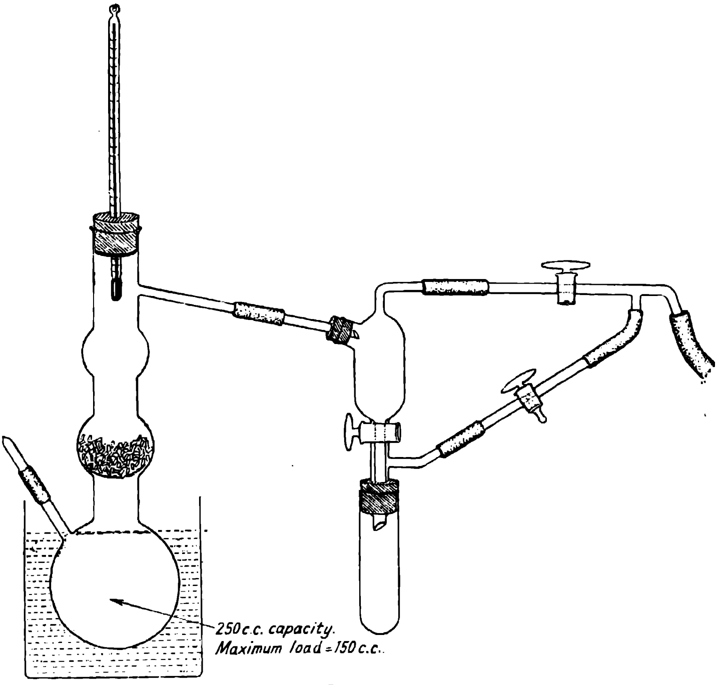


FIG. 6.

The intermediate bulb is filled to between one-half and (not more than) two-thirds of its capacity with small hollow metal cylinders (the small " eyelets " used for attaching papers, etc., together are very suitable); these are supported by a slip of thin copper gauze. When efficient distillation is proceeding these metal cylinders are covered with a film of condensed ester which drips back through the gauze, but over-condensation of too much liquid in this bulb causes turbulent motion in the ascending column of vapour and impairs the efficiency of the fractionation obtained. To prevent over-condensation due to radiation losses, the whole of the exposed neck from just above the lowest bulb to just below the junction of the side tube is wrapped in asbestos cloth.

The lowest bulb is provided with a side-arm for filling purposes only. Air or other gas is never drawn through this tube, which is kept closed by a solid tube connected by rubber tubing during distillation. Smooth ebullition is assisted by the provision of a liberal amount of fresh, finely broken porous tile.

The neck of the bulb is fitted with a rubber cork carrying a thermometer, the bulb of the latter being exactly opposite the side-arm of the flask. Below the rubber cork is fitted a thin disc (about $\frac{1}{8}$–$\frac{3}{16}$ inch) of good ordinary cork, which serves to protect the rubber from the solvent action of the hot, condensing ester vapours.

The lower bulb is immersed nearly completely (to the level shown in Fig. 6) in an oil bath constructed of thin metal, the temperature of which is maintained by a Bunsen burner, the gas-flow to which can be closely controlled. The temperature of the oil bath is so regulated that distillation proceeds steadily at a rate not exceeding about thirty drops per minute. (Control of the heating is best secured by placing a thermometer so that its bulb rests on the bottom of the oil bath. This gives a rapid and convenient indication of changes in the flow of heat from the gas flame to the oil; this is the essential factor in controlling the heating of the bulb. The mean temperature of the oil, as registered by a thermometer suspended in it, is not of direct importance from this point of view.) When distillation is proceeding normally at about 0·2 mm. pressure, the reading on the thermometer in the oil bath is usually about 50°, and should not be more than 70°, higher than that at the head of the column.

The ester-fractions are collected through a Perkin receiver in the ordinary way, so that a fraction may be removed without breaking the vacuum in the apparatus. Cylindrical receivers about 10 cm. in length made from stout, soft glass tubing are convenient for the collection of the ester-fractions.

Unless a large fraction of approximately known range is being collected for the purpose of refractionation, the weight of any one ester-fraction should not greatly exceed about 10 g., and may be as little as 2–3 g. Even when it is tolerably certain that a mixture of constant composition is distilling in large quantity, it is better not to exceed the amount stated: errors in the analytical determination of equivalents or iodine values are minimised if carried out on several small, rather than on one very large, fraction. The minimum weight of a fraction is determined simply by the minimum amount necessary for accurate determination of its analytical characteristics.

Normally, the unsaponifiable or non-fatty matter remains in the residual, undistilled ester fraction (which need not exceed 4–5 g.); its amount is determined by its removal from the alkaline solution obtained after determination of the apparent equivalent of the residual ester, followed by recovery of the fatty acids and re-determination of their equivalent. The amount of esters in r g. of a residual ester is then:

$$r \times \frac{(\text{equivalent of recovered fatty acids} + 14)}{\text{apparent equivalent of residual esters}}$$

Distillation of small quantities of mixed fatty esters from a simple bulb. Lovern [19] has described a modification of the above-mentioned technique to deal with cases in which only small amounts of fat or of the corresponding esters (down to 10 g.) are available.

> " A small plain distilling flask is used, with a bulb of 50 c.c. capacity and a side-tube let into the bulb as in the Willstätter flask. A slight constriction in the neck supports a spiral of copper wire, to act as a fractionating column. Quantities as small as 1 g. may be fractionated from this, the residues usually being no more than 0·4 to 0·5 g. Fractions are collected in receivers made from shortened test-tubes, and quantities as low as 0·3 g. may be collected and the saponification equivalent and iodine value determined. Iodine values on one-quarter of the usual quantity of material are easily performed by the use of proportionately smaller quantities of reagents and titration with more dilute thiosulphate. Equivalent determinations on as little as 0·1 g. of material may be carried out as follows: the fat is weighed into a shortened test-tube, 2 c.c. of N/2 alcoholic potash added and the mixture boiled for one hour under reflux with exclusion of carbon dioxide. The contents are washed out with 80 c.c. of neutral alcohol into a suitable flask and titrated with N/50 sulphuric acid. A good end-point at such dilution depends on the choice of a suitable indicator,

e.g. dibromothymoltetrachlorophthalein. This has a very small *p*H range (8·8 to 8·4) from deep blue to colourless, and after a little practice, satisfactory duplicates can be obtained. A blank determination is made as usual.

" Unfortunately, in the " micro "-method, it is often impossible to refractionate the fractions from the primary distillation, and this is probably the greatest source of error. In certain cases mixtures have to be taken as containing only two components for the composition to be calculated, and it is almost impossible to obtain only such fractions in one distillation, especially perhaps in this simpler distilling flask. Each fraction, however, will contain mainly two components, and in many cases only two." (*Lovern, loc. cit.*)

Distillation through heated fractionating columns. Use has been made by various workers in this field of a more elaborate fractionating column which can be heated to varying temperatures. By this means considerably sharper resolution of the components (especially those present in slight quantities) of mixed higher fatty esters can be effected than by the simpler apparatus described above, but the experimental procedure naturally becomes somewhat more complicated. On the other hand, the absence of need for refractionation of any primary fractions compensates largely for the increase in complexity of the technique and the extra time usually required for a single distillation when a more elaborate column is used.

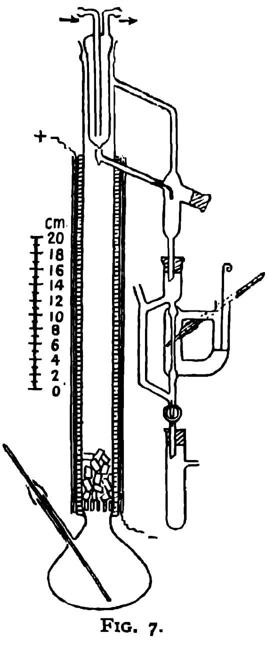


Fig. 7.

The first application of this device in the case of higher fatty esters appears to have been made in 1930 by Jantzen and Tiedcke,[20] who employed a heated column in order to secure effective separation of methyl arachidate, behenate, and lignocerate (from the saturated acids present in groundnut oil). They used a comparatively simple glass column (Fig. 7), packed with small aluminium rings and heated externally by three cylindrical electrically heated hot plates connected in series and enveloping the column ; the heating cylinders are lagged with four layers of asbestos. The head of the column is furnished with a water-cooled condenser, the condensate being collected into a tube leading to the receiver system. (The special type of receiver used by Jantzen and Tiedcke (Fig. 7) includes a device whereby the melting point of any given portion of the condensate can be determined during the course of the distillation.) The distilling flask may take up to 150 g. of esters, and the rate of distillation should not exceed about 5 drops per minute, with a reflux rate of about 25 drops per minute.

Longenecker [21a] applied to the fractional distillation of mixtures of higher fatty esters an electrically heated and packed column (referred to hereinafter as the " E.H.P. column ") of a type previously described by Whitmore and Lux,[21b] fitted with an arrangement for total reflux and adjustable distillate collection. The column and reflux-head is illustrated in Fig. 8, and the description which follows is taken from Longenecker (*loc. cit.*).

"The column is all glass (Pyrex) making the entire operation visible. It is 90 cm. in height ; the inside diameter is 17 mm. Single-turn glass helices [21c] were used to pack the column for a distance of 60 cm. The purpose of the

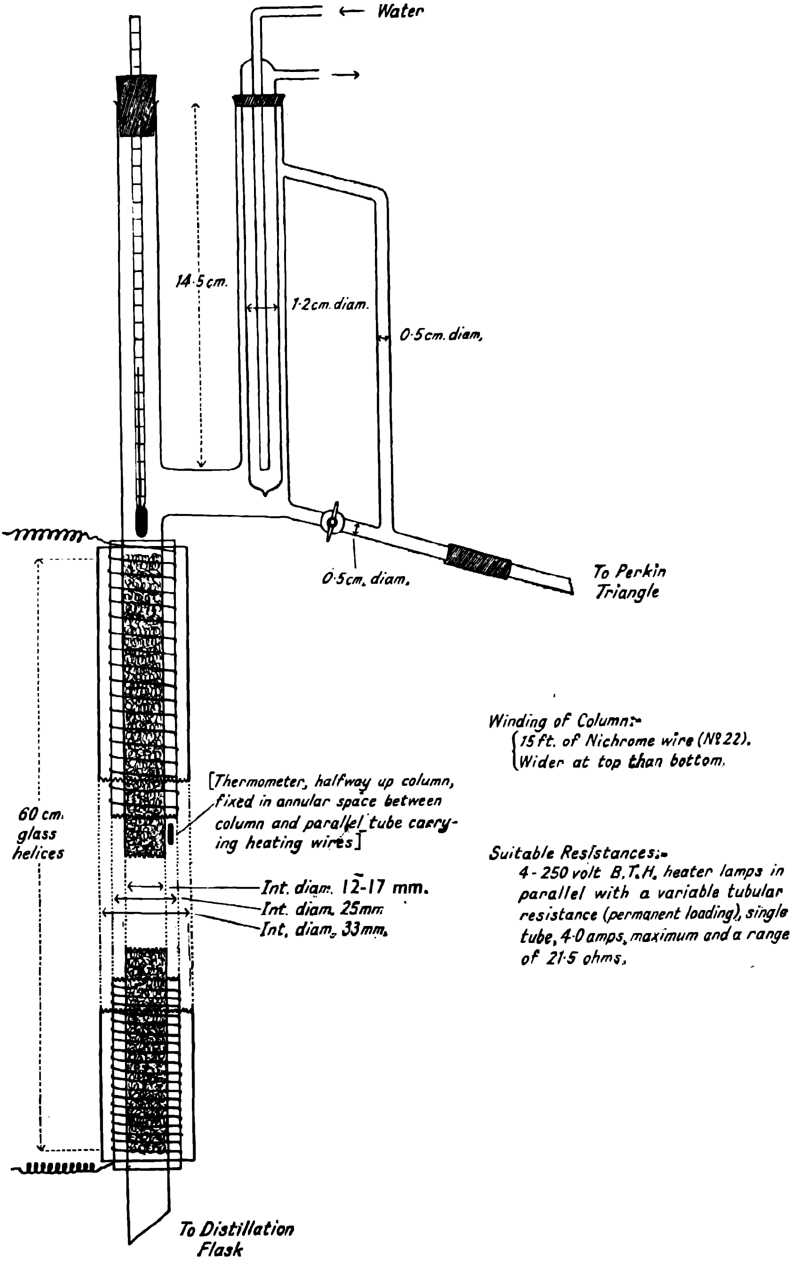

← Water
→
14·5 cm.
1·2 cm. diam.
0·5 cm. diam.
0·5 cm. diam.
To Perkin Triangle
Winding of Column:-
15 ft. of Nichrome wire (No. 22).
Wider at top than bottom.
[Thermometer, halfway up column, fixed in annular space between column and parallel tube carrying heating wires]
60 cm. glass helices
Int. diam. 12-17 mm.
Int. diam. 25 mm.
Int. diam. 33 mm.
Suitable Resistances:-
4 - 250 volt B.T.H. heater lamps in parallel with a variable tubular resistance (permanent loading), single tube, 4·0 amps. maximum and a range of 21·5 ohms.
To Distillation Flask

FIG. 8.

packing material and the effects of different types in the production of low H.E.T.P.[21d] (height equivalent to a theoretical plate) has been demonstrated by Fenske, Tongberg, and Quiggle.[21e]

"To reduce heat loss and maintain control of the conditions of the distillation, the column is electrically heated by 15 ft. of Nichrome wire (No. 22) wound on a piece of 25-mm. Pyrex tubing the length of the packed distance. This heating jacket is protected and insulated by a Pyrex tube, 33 mm. in thickness. Fine control on the temperature of the column (recorded on a thermometer inserted between the column and the electrically heated jacket) is suitably regulated by external fixed and variable resistances.

"At the top of the column is a still-head with an enclosed thermometer. The ascending vapours flow past its bulb to a condenser. Collection of the distillate is regulated by a stopcock (2 mm.) attached below the condenser, a separate connection providing for the maintenance of low pressures (or the release of pressure, depending on the conditions) when the stopcock is closed.

"The temperature of the vapour at the top of the column should at any time, except towards the end of a distillation, be an approximation of the boiling point of the material being collected. Under ideal conditions of operation of this column this temperature is an accurate index to the efficiency of the fractionation. The temperature rise for adjacent members of the fatty acid series is approximately 15–20°, depending on the pressure (0·1–2 mm.).

"For convenience, removable distillation flasks are used. Cork of good quality proved the best adaptor for the ester distillations after a trial of ordinary rubber stoppers, Duprene stoppers, and ground glass connections.

"Maximum efficiency is obtained by a regulation of the bath and column temperatures so that there is never a visible accumulation of liquid (' flooding ') in the packed length of the column. The rate of distillation, i.e. collection of condensate, is controlled by the stopcock in the still-head. The stopcock is closed at the beginning of a distillation and frequently during the collection of intermediate fractions (which are indicated by the temperature fluctuations in the still-head) to allow for the attainment of equilibrium between the vapour and liquid phases.

"An ester mixture obtained in the course of analysis of a relatively simple fat may be efficiently separated in the course of 4–5 hours (for about 50 g. of mixed esters) ; a more complex mixture (e.g. from milk or fish fats) may require 7–8 hours for the distillation of 50–60 g. of esters. Despite the somewhat prolonged period of heating, there is no evidence that residual unsaturated esters undergo more profound decomposition than when a simple Willstätter bulb is employed."

The quantity of esters which can be distilled through the E.H.P. column, using a 250 c.c. round-bottomed flask as container at the base of the column, ranges from 15–20 g. to a maximum load of about 150 g. The container is immersed as deeply as possible in an oil-bath, the heating of the bath being controlled by means of a thermometer with its bulb resting on the bottom of the bath (as described in the case of the Willstätter flask apparatus, p. 477). A useful alternative to an oil-bath consists in a bath constructed of moulded aluminium of about 1 cm. thickness.[22a] The lower part forms a hemispherical bowl, whilst the upper part is in two vertical sections moulded so as to surround the neck of the round-bottomed flask as well as its upper spherical portion. The two upper parts can be locked together, and fit, by a tongue and groove, on to the lower portion. With the internal diameter of the spherical part of the bath about 11 cm., a 500 c.c. or a 250 c.c. flask can be used with it ; the base of the distillation flask should not be in contact with the bottom of the aluminium bath, an air space completely separating bath from flask. The bath is directly heated at its base by a Bunsen flame. This type of bath has been found to give very uniform heating combined with almost complete absence of " bumping " in the heated liquid.

The amount of residual esters (ca. 4 g.) is no greater than in the case of the simpler apparatus, whilst if desired the residual undistilled esters in the containing flask can be removed separately after the operation, and the final esters which have distilled and condensed on the packing in the column (usually about 2 g.) can be separately recovered by washing out with ether, and treated as a separate, penultimate ester-fraction.

A somewhat similar, in some respects more elaborate, column than that discussed above has been described by Weitkamp and Brunstrum.[23] The fractionating column (4 feet long and 1 inch diameter) is heated electrically in four sections and packed with wire-gauze cones, which give efficient fractionation and very low liquid hold-up. It is claimed that the transition in boiling-point between successive homologues is sufficiently abrupt to obviate, for technical analytical purposes, the chemical determination of the equivalents of the fractions.

The effect of heat during the fractionation process upon unsaturated fatty esters has been considered by Norris *et al.*[24a] They find that esters of acids with three or fewer unconjugated double bonds are substantially unaffected, whilst those of more unsaturated polyethenoid (e.g. fish oil) acids are also little altered, although slight rearrangement to conjugated isomerides, followed by some dimerisation, may take place to a very small degree. Any material so altered appears in the residual undistilled esters. These authors came to the conclusion, however, that the changes induced in the course of a fairly prolonged fractional distillation were insignificant, and that the action of reagents (alkalies) and solvents during hydrolysis of the fats and their treatment prior to fractionation is a much more important potential source of structural alteration than any conditions encountered during fractional distillation in a vacuum. On the other hand, it should be pointed out that esters of conjugated higher fatty acids undergo polymerisation and/or cyclisation at the temperature at which they distil in heated fractionating columns of the above types, and that such esters (e.g. methyl elæostearates) cannot be distilled in a column of the " E.H.P." type without substantial alteration.[22b]

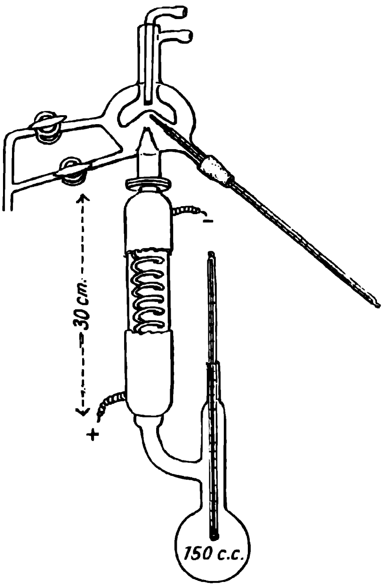
Norris and Terry [24b] have given data which shows that a fractionating column of the Podbielniak type is still more effective than the Whitmore-Lux column discussed above. They have also given precise boiling point data for different pressures as follows :

Pressure (mm.) :	1	2	5	10	20
Methyl myristate	114°	125°	143·5°	157·5°	172·5°
„ palmitate	136	149	166·5	180·5	196·5
„ stearate	155·5	170	189·5	204·5	222
„ oleate	152·5	166·6	186	201	218·5
„ linoleate	149·5	163	182·5	198	215

Baldwin and Longenecker [21f] have analysed known mixtures of methyl laurate, myristate, palmitate, stearate, oleate, linoleate and linolenate in the E.H.P. column without preliminary separation (linoleate and/or linolenate being determined spectrographically in the ester fractions) and found good accordance between their results and the known compositions of the mixtures, which contained some or all of the acids mentioned.

Other heated fractionating column devices have been used for higher fatty esters, most of which are designed for the distillation of very small quantities of material.

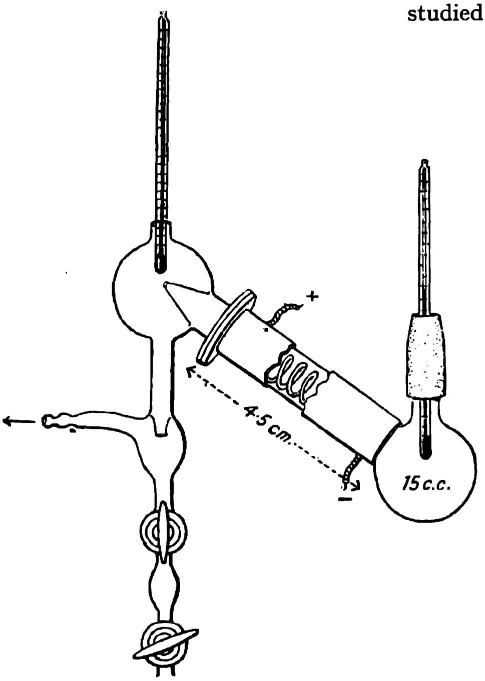
Diemair and Schmidt [25] have described two types of apparatus suitable for the distillation respectively of 5–30 g. and 0·5–5 g. of fatty esters or acids. The essential parts of the distilling columns are shown in Fig. 9 (*a*) and (*b*). In the apparatus for 5–30 g. of material (Fig. 9(*a*)) the (150 c.c.) distilling flask (of the Claisen type) is sealed to the column, which consists of a glass spiral in a cylindrical glass tube (30 cm. long) which is surrounded by an electrically heated wire enclosed in an asbestos sheath. The vapours from



(*a*)
Fig. 9.

the top of the spiral impinge through a jet (of internal diameter 2–3 mm.) on to the under surface of a water-cooled condensing bulb. The apparatus is operated in the vacuum (0·001 mm.) of a mercury vapour pump, and the rate of distillation must not exceed 1–1·5 g. per hour.

For distillation of 0·5–5 g. of material the modified form shown in Fig. 9 (*b*) is recommended by Diemair and Schmidt. In this case the flask (15 c.c.) is directly connected to a shorter column (4·5 cm. long), the latter being set at an angle, instead of vertically; the vapours are not in this instance cooled by a water-condenser. Distillation of one gram of esters, etc., occupies 4–5 hours and fractions of 0·1 g. may be separately collected. For the exact measurements and working details of the Diemair and Schmidt apparatus their original communication [25] should be carefully studied.



(*b*)
Fig. 9.

Schoenheimer and Rittenberg [26] have given details of another form of apparatus (Fig. 10), which they have used successfully for the separation by fractional distillation of small quantities (1–3 g.) of higher fatty esters. The distinctive feature of their apparatus is that the distilling vapours pass up through an external, and then down through an internal, concentric space before finally passing upwards through the central column (in which a close-fitting wire helix is placed to aid fractional separation).

The whole column is in glass, and is sealed to the distilling flask of 10 c.c. capacity. The outermost tube of the column is wrapped, first with copper foil, then with thin asbestos paper, and heated electrically by a nichrome wire conductor wrapped round this layer of asbestos; the whole exterior is finally lagged heavily with asbestos. Condensed liquid from the inner concentric tube and the innermost tube of the fractionating column can run back to the distilling flask from the base of the inner concentric tube; but in this apparatus (as in that of Diemair and Schmidt) there is no special device for reflux at the head of the fractionating column. The distilling flask is heated in a Wood's metal bath and the pressure is maintained as near to 0·05 mm. as possible (but not below). The rate of heating is adjusted so that 30–50 drops return to the flask for each drop collected at the receiver; not more than 0·15–0·20 g. should be collected per hour, and separated fractions from 0·1 g. upwards may conveniently be collected.

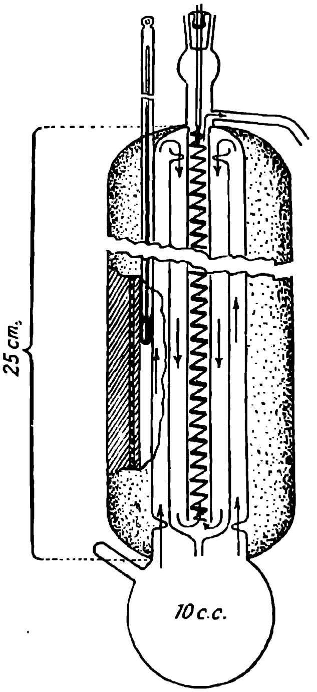


FIG. 10.

Here, again, Schoenheimer and Rittenberg's original paper [26] should be consulted for more complete details of the dimensions, construction, and working of this apparatus.

Klem [27] has given a preliminary account of three sizes of vacuum distillation apparatus suitable for distilling quantities of from 5 g. to 500 g. of higher fatty esters, etc. Each apparatus is equipped with an electrically heated flask, column and column top, each of which can be regulated independently of the other. The temperature is controlled by thermocouples with an accuracy of ±0·5° C. The columns are fitted internally with spirals of monel metal or stainless steel and are furnished with a high-vacuum jacket of Durandl glass fused to the column. On the outside, the columns are insulated with asbestos fitted with mica windows. The electric heating spiral is wound round a glass tube outside the vacuum jacket. Further details concerning the apparatus are promised in a later publication.

TYPICAL ESTER-FRACTIONATION DATA OBTAINED WITH THE SIMPLE WILLSTÄTTER FLASK (p. 476) AND THE "E.H.P. COLUMN" (p. 479) TYPES OF APPARATUS

It may be useful to quote in detail a few examples of the ester-fractionation data obtained for different kinds of fats. This has been done in Tables 105–109 (pp. 486–503), which include in addition the composition of each ester-fraction (deduced from the equivalents, iodine values and, where necessary, equivalents of the saturated esters present). The method by which the composition of the total acids of a fat is derived from that of the ultimate ester-fractions will thus be evident. Various considerations affecting the mode of calculation of the components of each ester-fraction are dealt with in the next section of this chapter (pp. 484–485, 504–512).

The fats selected for illustrative purposes are instances studied in the writer's laboratory at the University of Liverpool, and include:

Table 105.—A cow milk fat (to illustrate the case in which lower (steam-volatile) fatty acids accompany the higher fatty acids).

Table 106.—A pig inner back fat. This is typical of the more simple mixtures of acids, present in many animal and vegetable fats, and is chosen for the present purpose because the esters of the "liquid" acids were fractionated both from a Willstätter flask and also by means of the "E.H.P. column" (p. 479). The data show that substantially the same figures are obtained by the use of either the simpler or the more elaborate fractioning device.

Tables 107 and 108.—A hydrogenated whale oil of iodine value 88·6 and a whale oil of iodine value 108·0. These are typical of the most complex mixtures of higher saturated and unsaturated fatty acids likely to be encountered. The whale oil data (Table 108) also illustrate the use of lithium salt acetone separation for highly unsaturated acids prior to the lead-salt alcohol separation. The data for both these oils are referred to in some detail when dealing (pp. 505–509) with the calculation of the more complex types of ester-fractions.

Table 109.—A seed-oil of the more unsaturated type (rubber seed oil). This example illustrates, *inter alia*, the preliminary partial separation of the mixed fatty acids by low-temperature crystallisation, instead of by lead-salt separation. It also shows the use of spectrographic determination of linoleic and linolenic acids (after isomerisation by alkali) in the evaluation of mixtures of oleic, linoleic, and linolenic acids.

SOME FEATURES OF THE CALCULATION OF THE COMPOSITION OF INDIVIDUAL ESTER-FRACTIONS

The ideal case, in the ester-fractionation procedure for the analysis of a mixture of fatty acids, is to produce a series of ester-fractions, each of which shall contain not more than two saturated esters, accompanied by not more than one unsaturated ester (or, at least, esters of unsaturated acids with the same number of carbon atoms). The composition of such fractions can be directly calculated from their saponification equivalents and iodine values. This holds for many fats in which the only unsaturated components belong to the C_{18} series of acids (oleic, or, oleic with linoleic or linolenic, etc.). When, as is usually the case, both oleic and linoleic (or linolenic) acids are present, the mean iodine value of the C_{18} unsaturated esters can be determined and the assumption made that these esters distil throughout in the same proportions; this is not absolutely correct, but the error thereby introduced is usually negligible.*

When linolenic acid accompanies linoleic and oleic acid, as is the case in many liquid seed fats, it is necessary (having arrived at the total amount of unsaturated C_{18} acids in individual ester-fractions, or in the whole of a fractionated ester mixture) to determine the amount of each of the three unsaturated acids present. This may be best carried out from spectrographic measurement of the conjugated di- and tri-ethenoid acids produced by controlled alkali-isomerisation of the linoleic and linolenic acids present [28] (*cf.* Chapter IV, pp. 138, 154); or, if a spectrograph is not available, thiocyanometric analysis may be resorted to, the empirically agreed values [29] (*cf.* Chapter IV, p. 138) for the thiocyanogen values of linoleic and linolenic acids being employed. Of course, when linoleic acid is the only polyethenoid acid present, a complete determination of ester-fractions which contain, for example, two saturated acids, one mono-ethenoid acid, and linoleic acid, or one saturated and two mono-ethenoid acids with linoleic acid, can be made from the iodine value and saponification equivalent in conjunction with the above spectrographic or thiocyanometric determination of linoleic acid.

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* The boiling point of methyl linoleate is very slightly below that of methyl oleate. Even in distillation from a Willstätter flask, the ratio of linoleate to oleate in the lowest boiling fractions is slightly higher than in the main C_{18}-unsaturated ester fractions. When the electrically heated fractionation column (p. 479) is employed, the partial concentration of methyl linoleate in the lower boiling fractions is somewhat more marked. Here, with mixtures containing high proportions of oleic and linoleic esters, it is frequently observed that the pure C_{18} unsaturated ester mixtures which come over first have a definitely higher iodine value than those which follow. (This does not happen to have occurred in the instances cited in Tables 105–109.) In such cases the iodine value of the first pure C_{18} ester mixture obtained may be used as an approximate mean unsaturation value for any C_{18} esters in immediately preceding fractions, whilst of course each succeeding pure C_{18} ester-fraction obtained is calculated to oleic and linoleic esters according to its own iodine value.

In some other fats, especially those from aquatic sources, the mixture of unsaturated acids (especially in the C_{20} and C_{22} series) is complex, the constitution of many of the polyethenoid acids is still uncertain, and neither of the methods mentioned can yet be applied in these instances. In cases of this kind, where unsaturated acids of the C_{14}, C_{16}, C_{20}, C_{22}, and even C_{24} series accompany those of the C_{18} group, it becomes necessary to adopt a different method of evaluation of the ester-fractions, some of which then contain two saturated esters with esters of unsaturated acids belonging to two series (e.g. C_{16} and C_{18}, or C_{18} and C_{20}, etc.). Here it may become necessary to know the amount or, at least, the equivalent of the *saturated* esters present, or alternatively (providing that the saturated and unsaturated components belong only to *two* homologous series, e.g. C_{16} and C_{18}) to determine the equivalent of the ester-fraction after it has been completely hydrogenated. It may happen, however, that mixtures of *three* groups of the homologous series are present (e.g. myristic, palmitic, hexadecenoic and unsaturated C_{18} esters), so that the hydrogenated products include esters of three saturated acids. Here the hydrogenation method fails, since the equivalent of the hydrogenated esters does not serve for the determination of all the fatty acids present in the hydrogenated ester-fraction.

It seems better, therefore, to determine either the amount and/or the equivalent of the saturated esters present in the ester-fractions concerned. In a number of instances (usually where the proportion of unsaturated esters is low in comparison with that of the saturated esters, or *vice versa*) it has been found safe to assume that the equivalent of both saturated and unsaturated parts of the ester-fraction are the same. As described later (p. 506), the evaluation can then be effected on the basis only of the iodine value and saponification equivalent of the ester-fraction.

Determination of saturated esters present in certain ester-fractions. A weighed quantity of the ester-fraction is dissolved in anhydrous acetone (10 vols.) and finely powdered potassium permanganate (passing a 50-mesh sieve) is added at such a rate that the mixture is kept in gentle ebullition. When the amount of permanganate present is four times that of the esters taken, the mixture is refluxed for some hours. The bulk of the acetone is then removed by distillation, and the residual solid matter powdered with about its own weight of powdered sodium bisulphite, after which it is dropped into dilute sulphuric acid solution, and decolorisation of manganic oxides present is completed by heating. The organic compounds present are extracted with ether, and the ether solution washed repeatedly with potassium carbonate solution, and then with water, in order to remove all acidic products of oxidation.

If the iodine value of the unattacked (neutral) portion of the oxidised esters exceeds 1, it is necessary to repeat the oxidation process once, or even twice, in

TABLE 105. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF A COW MILK FAT* (S. Paul)

In this analysis, the steam-volatile acids were dealt with as described on p. 467, whilst the esters of the " solid " and of the " liquid " acids were distilled through the electrically-heated and packed (" E.H.P.") column described by Longenecker.[21a]

The original fat had saponification equivalent 252·9, iodine value 46·9, and the mixed fatty acids from about 250 g. of the fat yielded 13·2 g. (5·6 per cent.) steam-volatile and 224·2 g. (94·4 per cent.) of non-steam-volatile acids; the latter yielded 46·0 per cent. of " solid " acids and 54·0 per cent. of " liquid " acids.

(a) *Fractional Distillation of the Steam-volatile Acids* (*as Acids*)

	Vol. c.c.	c.c. N/10 KOH	Wt. g.	B.P.	S.E.	I.V.		Butyric	Hexanoic	Octanoic	Oleic
Ether-extd. aq. soln.	4,570	192·0	1·69					1·69	—	—	—
Ether ex vol. acids	2,500	11·77	0·10					0·10	—	—	—
Fractions	g.			Atm.							
V1	115·8	15·05	(0·13)	35–100°				0·13	—	—	—
V2	1·33	100·6	(0·89)	100–160°				0·89	—	—	—
V3	1·26		(1·22)	160–164°	91·2†	—		1·22	—	—	—
V4			1·63	164°	90·5	—		1·44	0·19	—	—
V5			1·59	164–170°	91·8	—		1·32	0·27	—	—
V6			1·53	170–172°*	95·0	—		1·06	0·47	—	—
				15 mm.							
V7			2·46	76–114°*	103·8	—		0·91	1·55	—	—
V8			1·94	Residue	154·6	20·2		—	0·35	1·15	0·44
			13·18				Totals	8·76	2·83	1·15	0·44
							Per cent. acids	66·5	21·5	8·7	3·3

* Falling.

† Calculated as butyric acid+water.

(b) *Fractional Distillation of Methyl Esters of the " Solid " Acids*

(62·15 g. distilled through " E.H.P. column ")

No.	G.	Temperature of: Oil Bath	Column: Middle	Column: Head	S.E.	I.V.	Calculated Composition of Ester-fractions: Saturated C_{12}	C_{14}	C_{16}	C_{18}	as C_{20}	Unsaturated C_{12}	C_{14}	C_{16}	Oleic
S1	1·51	197–199°	154–160°	94–98°	214·8	1·1	1·41	0·09	—	—	—	0·01	—	—	—
S2	3·38	199–204°	160–164°	98°	244·1	0·9	—	3·07	0·28	—	—	—	0·02	0·01	—
S3	1·94	204°	164–170°	98–114°	259·0	1·4	—	0·70	1·21	—	—	—	0·01	0·02	—
S4	8·56	204–211°	170°	114°	264·0	1·0	—	1·66	6·81	—	—	—	0·01	0·08	—
S5	9·33	211–214°	170–174°	114–118°	265·7	0·9	—	1·29	7·95	—	—	—	0·01	0·08	—
S6	8·00	214–221°	174–194°	118–120°	267·7	3·0	—	0·56	7·19	—	—	—	—	0·25	—
S7	9·37	221–226°	194–212°	120–134°	290·9	24·7	—	—	2·07	4·60	—	—	—	—	2·70
S8	8·43	226–228°	212–230°	134–138°	293·6	22·9	—	—	1·06	5·12	—	—	—	—	2·25
S9	6·24	228–235°	230–236°	138—falling	293·6	20·4	—	—	0·78	3·98	—	—	—	—	1·48
S10	5·23	Residue	Residue	Residue	303·4*	19·6	—	—	—	2·81	1·23	—	—	—	1·19
Weights	61·99						1·41	7·37	27·35	16·51	1·23	0·01	0·05	0·44	7·62
Per cent. Esters							2·3	11·9	44·1	26·6	2·0	Trace	0·1	0·7	12·3
Per cent. Acids							2·2	11·8	44·1	26·8	2·0	Trace	0·1	0·7	12·3

(All unsaturated esters taken as mono-ethenoid.)

* S10, Esters freed from unsaponifiable matter, S.E. 303·0.

TABLE 105. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF A COW MILK FAT* (S. Paul)—*continued*

(c) *Fractional Distillation of Methyl Esters of the " Liquid " Acids*

(117·3 g. distilled through " E.H.P. column ")

		Temperature of					Calculated Composition of Ester-fractions												
		Oil Bath	Column				Saturated					Unsaturated							
No.	G.		Middle	Head	S.E.	I.V.	C_8	C_{10}	C_{12}	C_{14}	C_{18}	C_{10}	C_{12}	C_{14}	C_{16}	Ol.	Lin.	C_{20-22}	N-S
L1	1·16	150–170°	86–100°	36–56°	174·9	9·6	0·41	0·67	—	—	—	0·08	—	—	—	—		—	—
L2	1·60	170–184°	100–110°	56–58°	181·2	13·5	0·25	1·19	—	—	—	0·16	—	—	—	—		—	—
L3	1·52	184–192°	110–134°	58–74°	203·4	8·4	—	0·49	0·93	—	—	0·03	0·07	—	—	—		—	—
L4	1·59	192–194°	134–140°	74–84°	209·4	8·4	—	0·22	1·26	—	—	0·01	0·10	—	—	—		—	—
L5	1·69	194–198°	140–148°	84–100°	227·4	18·0	—	—	0·70	0·72	—	—	0·11	0·16	—	—		—	—
L6	7·09	198–210°	148–170°	100–102°	235·4	16·8	—	—	1·28	4·71	—	—	0·16	0·94	—	—		—	—
L7	4·98	210–214°	170–190°	102–120°	256·4	40·0	—	—	—	1·36	1·61	—	—	0·78	1·23	—		—	—
L8	4·91	214–225°	190–204°	120–124°	267·9	60·4	—	—	—	0·13	1·65	—	—	—	3·13	—		—	—
L9	3·69	225–226°	204–210°	124–135°	276·9	75·4	—	—	—	—	0·81	—	—	—	1·68	1·20		—	—
L10	9·42	226°	210–218°	135–138°	290·3	89·4	—	—	—	—	0·93	—	—	—	—	8·49		—	—
L11	10·56	226–225°	218°	138°	291·6	93·8	—	—	—	—	0·57	—	—	—	—	9·99		—	—
L12	11·46	225–227°	218–220°	138°	292·5	94·4	—	—	—	—	0·55	—	—	—	—	10·91		—	—
L13	12·41	227°	220–222°	138–140°	291·7	94·9	—	—	—	—	0·54	—	—	—	—	11·87		—	—
L14	11·47	227–225°	222°	140–142°	292·5	95·1	—	—	—	—	0·47	—	—	—	—	11·00		—	—
L15	11·64	225–230°	222–230°	142–146°	292·0	96·2	—	—	—	—	0·35	—	—	—	—	11·29		—	—
L16	10·24	230–234°	230°	146°	293·2	98·5	—	—	—	—	0·07	—	—	—	—	10·17		—	—
L17	5·39	234–250°	230–238°	146—falling	293·2	99·2	—	—	—	—	—	—	—	—	—	5·39		—	—
L18	6·32	Residue	Residue	Residue	331·8*	110·9*	—	—	—	—	—	—	—	—	—	4·15		1·65	0·52
	117·14																		
Weights							0·66	2·57	4·17	6·92	7·55	0·28	0·44	1·88	6·04	71·45	13·01	1·65	0·52
Per cent. Esters							0·6	2·2	3·6	5·9	6·4	0·2	0·4	1·6	5·2	61·0	11·1	1·4	0·4
Per cent. Acids							0·6	2·1	3·5	5·9	6·4	0·2	0·4	1·6	5·2	61·2	11·1	1·4	0·4

L18, Esters freed from unsaponifiable matter (" N–S "), S.E. 304·7, I.V. 100·0.

(C_{18} unsatd. esters taken as S.E. 295·7, I.V. 99·2.)
(C_{20-22} " " " S.E. 330·0.)

(d) *Calculated Composition of Total Milk Fat Acids*

	VOLATILE ACIDS	ACIDS NON-VOLATILE IN STEAM			FATTY ACIDS (EXCLUDING UNSAPONIFIABLE)	
ACID	(5·6 PER CENT.)	“SOLID” ACIDS S (43·4 PER CENT.)	“LIQUID” ACIDS L (51·0 PER CENT.)	TOTAL	PER CENT. (WT.)	PER CENT. (MOL.)
Saturated:						
Butyric	3·72	—	—	3·72	3·7	10·2
Hexanoic	1·20	—	—	1·20	1·2	2·5
Octanoic	0·49	—	0·28	0·77	0·8	1·3
Decanoic	—	—	1·09	1·09	1·1	1·5
Lauric	—	0·97	1·79	2·76	2·8	3·3
Myristic	—	5·12	2·99	8·11	8·1	8·6
Palmitic	—	19·13	3·28	22·41	22·5	21·1
Stearic	—	11·61	—	11·61	11·6	9·9
Arachidic	—	0·87	—	0·87	0·9	0·7
Unsaturated:						
Decenoic	—	—	0·12	0·12	0·1	0·2
Dodecenoic	—	0·01	0·19	0·20	0·2	0·2
Tetradecenoic	—	0·03	0·81	0·84	0·8	0·9
Hexadecenoic	—	0·31	2·64	2·95	3·0	2·8
Octadecenoic	0·19	5·35	31·18	36·72	36·8	31·4
Octadecadienoic	—	—	5·68	5·68	5·7	4·9
C_{20-22} unsaturated	—	—	0·72	0·72	0·7	0·5
Unsaponifiable	—	—	0·23	0·23	—	—

Analytical Characteristics of Original Milk Fat (including Unsaponifiable Matter)

	CALCULATED FROM DATA IN (*d*) (*above*)	DETERMINED ON ORIGINAL FAT
Saponification equivalent	253·8	252·9
Iodine value	46·7	46·9

TABLE 106. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF A PIG INNER BACK FAT* (W. H. Pedelty)

In this analysis, the esters of the " solid " acids were distilled from a Willstätter flask, but those of the " liquid " acids were divided into two parts, one of which was distilled from a Willstätter flask and the other through the electrically heated (" E.H.P.") column. A comparison of the results of each method of fractionation can therefore be made.

The original fat had saponification equivalent 285·4, iodine value 54·3. The mixed acids (283 g.) from 302 g. of the fat yielded 44·8 per cent. of " solid " acids and 55·2 per cent. of " liquid " acids. (The weight of acids used in this analysis was large in order to permit of the duplicate fractionation of the " liquid " esters. For fats of this relatively simple type, the acids from 80–150 g. of fat are ample for an ester-fractionation analysis of the kind illustrated here.)

(a) *Fractional Distillation of Methyl Esters of the " Solid " Acids*

(121·1 g. distilled from a Willstätter flask)

No.	G.	Temperature of		S.E.	I.V.		Saturated			Oleic	N-S
		Oil Bath	Column Head				C_{14}	C_{16}	C_{18}		
S1	1·96	162–168°	104–120°	269·1	0·9		0·06	1·88	—	0·02	—
S2	2·87	168–174°	120–132°	269·9	1·0		0·01	2·83	—	0·03	—
S3	6·26	174–178°	132–133°	271·3	1·0		—	5·97	0·22	0·07	—
S4	8·97	178–187°	133–137°	272·1	1·0		—	8·18	0·69	0·10	—
S5	13·26	187–191°	137–141°	272·4	1·1		—	12·06	1·03	0·17	—
S6	14·43	191°	141°	273·4	1·3		—	12·54	1·67	0·22	—
S7	11·92	191–197°	141–143°	275·7	1·4		—	9·24	2·49	0·19	—
S8	11·59	197–201°	143–149°	279·1	2·0		—	7·56	3·76	0·27	—
S9	13·51	201–205°	149–153°	282·0	2·5		—	7·37	5·75	0·39	—
S10	12·02	205–210°	153–154°	287·1	3·1		—	4·32	7·27	0·43	—
S11	4·62	210–212°	154–159°	292·8	3·8		—	0·76	3·66	0·20	—
S12	5·84	212–214°	159–163°	293·6	4·1		—	0·84	4·72	0·28	—
S13	6·85	214–235°	163—falling	296·8	4·1		—	0·25	6·27	0·33	—
S14	6·34	Residue	Residue	301·2*	7·0*		—	0·04	5·73	0·50	0·07
	120·44					Weights	0·07	73·84	43·26	3·20	0·07
						Per cent. Esters	Trace	61·3	35·9	2·7	Trace
						Per cent. Acids	Trace	61·2	36·0	2·7	Trace

* S14, Esters freed from unsaponifiable matter, S.E. 298·1, I.V. 6·6.

(b) *Fractional Distillation of Methyl Esters of the " Liquid " Acids*

(i) *From a Willstätter flask* (79·26 g. esters)

The first primary fraction was collected so as to include nearly all the esters of acids below the C_{18} group, and was subsequently refractionated.

PRIMARY FRACTIONATION

		TEMPERATURE OF				SATURATED		UNSATURATED				
NO.	G.	OIL BATH	COLUMN HEAD	S.E.	I.V.	C_{14}	C_{16}	C_{16}	OL.	LIN.	C_{20-22}	N-S
L1	27·40	180–195°	113–149°	285·6	83·1	0·68†	4·17†	4·15†	18·40†		—	—
L2	8·28	195–197°	149–150°	290·5	93·7	—	0·44	—	7·84		—	—
L3	9·51	197–198°	150°	294·0	95·0	—	0·38	—	9·13		—	—
L4	8·86	197–210°	150–151°	294·8	96·7	—	0·21	—	8·65		—	—
L5	6·73	210–215°	151–153°	295·1	98·4	—	—	—	6·73		—	—
L6	5·20	215°	153–157°	295·5	99·8	—	—	—	5·20		—	—
L7	4·39	215–217°	157–160°	297·1	102·6	—	—	—	4·19		0·20	—
L8	5·06	217–220°	160–168°	299·1	107·2	—	—	—	4·51		0·55	—
L9	3·62	Residue	Residue	321·9*	132·4*	—	—	—	2·38		1·06	0·18
	79·05											
Weights						0·68	5·20	4·15	56·86	10·17	1·81	0·18
Per cent. Esters						0·9	6·6	5·2	71·9	12·9	2·3	0·2
Per cent. Acids						0·9	6·5	5·2	72·0	12·9	2·3	0·2

(C_{18} unsatd. esters taken as S.E. 295·7, I.V. 99·0.)
(C_{20-22} unsatd. esters taken as S.E. 330·0.)

* L9, Esters freed from unsaponifiable matter, S.E. 305·5, I.V. 125·5.
† L1, Components calculated from results of refractionation (below).

REFRACTIONATION OF ESTER-FRACTION L1

		TEMPERATURE OF				SATURATED		UNSATURATED				
NO.	G.	OIL BATH	COLUMN HEAD	S.E.	I.V.	C_{14}	C_{16}	C_{16}	OL.	LIN.	C_{20-22}	N-S
L11	1·82	160–170°	90–129°	258·4	51·3	0·60	0·24	0·98	—		—	—
L12	3·09	170–173°	129–132°	273·6	67·4	—	0·92	1·57	0·60		—	—
L13	3·09	173–186°	132–135°	279·9	75·5	—	0·69	1·05	1·35		—	—
L14	3·82	186–190°	135–150°	286·9	86·6	—	1·16	0·06	2·60		—	—
L15	4·42	190–192°	150–156°	288·7	90·4	—	0·38	—	4·04		—	—
L16	4·29	192–210°	156—falling	291·2	93·5	—	0·24	—	4·05		—	—
L17	3·62	Residue	Residue	293·2	97·6	—	0·05	—	3·57		—	—
	24·15											
Weights						0·60	3·68	3·66	16·21		—	—
Per cent. Esters						2·5	15·2	15·2	67·1		—	—

TABLE 106. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF A PIG INNER BACK FAT* (W. H. Pedelty)—*continued*

(b) *Fractional Distillation of the Methyl Esters of the "Liquid" Acids*—continued

(ii) *Through the "E.H.P. Column"* (73·76 g. esters)

No.	G.	Temperature of: Oil Bath	Column: Middle	Column: Head	S.E.	I.V.	Calculated Composition of Ester-fractions: Saturated C_{14}	Saturated C_{16}	Unsaturated C_{14}	Unsaturated C_{16}	Ol.	Lin.	C_{20-22}	N-S
L1	0·98	200–208°	160–168°	93–113°	234·8	13·5	0·86	—	0·12	—	—		—	—
L2	0·90	208–210°	168–178°	113–120°	247·8	29·6	0·41	0·24	0·25	—	—		—	—
L3	1·59	210–212°	178–180°	120–126°	267·9	54·2	0·05	0·63	—	0·91	—		—	—
L4	1·83	212–220°	180–187°	126–127°	270·1	55·0	—	0·77	—	0·97	0·09		—	—
L5	1·62	220°	187–188°	127–133°	275·4	59·8	—	0·61	—	0·59	0·42		—	—
L6	2·82	220–213°	188–196°	133–135°	282·1	74·4	—	0·67	—	0·70	1·45		—	—
L7	2·56	213–220°	196–200°	135–140°	289·4	92·8	—	0·15	—	0·40	2·01		—	—
L8	7·29	220–225°	200–210°	140°	291·3	96·4	—	0·19	—	—	7·10		—	—
L9	9·80	225°	210–208°	140–143°	294·2	97·1	—	0·19	—	—	9·61		—	—
L10	13·31	225°	208°	143–144°	294·6	97·7	—	0·17	—	—	13·14		—	—
L11	14·00	225°	208–212°	144°	295·2	99·0	—	—	—	—	14·00		—	—
L12	11·28	225–230°	212°	144–145°	295·6	99·9	—	—	—	—	11·28		—	—
L13	2·25	230–250°	212–240°	145–152°	301·9	104·4	—	—	—	—	1·81		0·44	—
L14	2·77	Residue	Residue	Residue	330·2*	155·6*	—	—	—	—	0·91		1·75	0·11
Weights	73·00						1·32	3·62	0·37	3·57	52·44	9·38	2·19	0·11
Per cent. Esters							1·8	5·0	0·5	4·9	71·8	12·8	3·0	0·2
Per cent. Acids							1·8	4·9	0·5	4·9	71·9	12·8	3·0	0·2

* L14, Esters freed from unsaponifiable matter, S.E. 317·4.

(C_{18} unsatd. esters taken as S.E. 295·7, I.V. 99·0.)
(C_{20-22} unsatd. esters taken as S.E. 330·0.)

(c) *Calculated Composition of Total Pig Inner Back Fat Acids*

(i) *All distillations from a Willstätter flask*

ACID	"SOLID" ACIDS S (44·8 PER CENT.)	"LIQUID" ACIDS L (55·2 PER CENT.)	TOTAL	FATTY ACIDS (EXCLUDING UNSAPONIFIABLE) PER CENT. (WT.)	PER CENT. (MOL.)
Myristic	0·03	0·47	0·50	0·5	0·6
Palmitic	27·41	3·62	31·03	31·1	33·1
Stearic	16·14	—	16·14	16·2	15·5
Hexadecenoic	—	2·88	2·88	2·9	3·1
Oleic	1·19	39·73	40·92	41·0	39·7
Linoleic	—	7·10	7·10	7·1	6·9
C_{20-22} unsaturated	—	1·27	1·27	1·3	1·1
Unsaponifiable	0·03	0·13	0·16	—	—

(ii) *Esters of " solid " acids distilled from a Willstätter flask*
Esters of " liquid " acids distilled through " E.H.P. column "

ACID	"SOLID" ACIDS S (44·8 PER CENT.)	"LIQUID" ACIDS L (55·2 PER CENT.)	TOTAL	FATTY ACIDS (EXCLUDING UNSAPONIFIABLE) PER CENT. (WT.)	PER CENT. (MOL.)
Myristic	0·03	0·99	1·02	1·0	1·2
Palmitic	27·41	2·73	30·14	30·1	32·2
Stearic	16·14	—	16·14	16·2	15·5
Tetradecenoic	—	0·28	0·28	0·3	0·3
Hexadecenoic	—	2·69	2·69	2·7	2·9
Oleic	1·19	39·65	40·84	40·9	39·6
Linoleic	—	7·10	7·10	7·1	6·9
C_{20-22} unsaturated	—	1·67	1·67	1·7	1·4
Unsaponifiable	0·03	0·09	0·12	—	—

Analytical Characteristics of Original Pig Inner Back Fat (including Unsaponifiable Matter)

	CALCULATED FROM DATA IN (c) (*above*) (i)	(ii)	DETERMINED ON ORIGINAL FAT
Saponification equivalent	285·9	285·6	285·4
Iodine value	52·7	53·6	54·3

TABLE 107. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF A HYDROGENATED WHALE OIL* (J. T. Terleski)

The hydrogenated whale oil had iodine value 88·6. The mixed acids (381·3 g.) from 400 g. of the fat yielded 23·1 per cent. of " solid " acids and 76·9 per cent. of " liquid " acids.

All fractionations in this analysis were from a Willstätter flask.

(a) *Fractional Distillation of Methyl Esters* (80·9 *g.*) *of the* " *Solid* " *Acids*

						Calculated Composition of Ester-fractions						
						Saturated				Unsaturated (Mono-ethenoid)		
No.	G.	Temperature at Head of Flask	S.E.	I.V.	Saturated Esters S.E. (Found)	C_{14}	C_{16}	C_{18}	C_{20}	C_{18}	C_{20}	C_{22}
S1	7·64	118–121°	251·6	2·1	—	5·01	2·44	—	—	0·19	—	—
S2	8·04	118°	254·4	2·4	—	4·40	3·42	—	—	0·22	—	—
S3	6·25	118°	258·4	3·0	—	2·59	3·44	—	—	0·22	—	—
S4	7·81	118–119°	261·9	3·5	—	2·36	5·13	—	—	0·32	—	—
S5	9·88	119–123°	268·3	4·2	—	0·91	8·49	—	—	0·48	—	—
S6	9·49	123–125°	273·8	6·1	—	—	7·96	0·86	—	0·67	—	—
S7	9·58	125°	276·1	8·3	274·1	—	7·31	1·34	—	0·93	—	—
S8	8·88	125–128°	282·7	14·7	280·0	—	4·56	2·79	—	1·50	0·03	—
S9	12·19	Residue	315·2	44·3	302·4	—	—	4·37	0·89	—	6·46	0·47
	79·76				Weights	15·27	42·75	9·36	0·89	4·53	6·49	0·47
					Per cent. Esters	19·2	53·6	11·7	1·1	5·7	8·1	0·6
					Per cent. Acids	19·1	53·5	11·8	1·1	5·7	8·2	0·6

(b) *Fractional Distillation of Methyl Esters* (288·4 g.) *of the " Liquid " Acids*

	PRIMARY FRACTIONATION					CALCULATED COMPOSITION OF ESTER-FRACTIONS							
						SATURATED		UNSATURATED					
No.	G.	TEMPERATURE AT HEAD OF FLASK	S.E.	I.V.		C_{14}	C_{16}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	N-S
L1	17·01	112–121°	253·7	51·5		5·86	2·26	2·98	5·91	—	—	—	—
L2	69·85	121–131°	268·7	73·6		8·41	8·69	4·51	32·14	15·80	0·30	—	—
L3	72·24	131–138°	287·2	95·1		—	2·31	—	20·97	44·90	4·06	—	—
L4	67·25	138–142°	299·7	110·9		—	0·04	—	1·57	53·96	11·56	—	0·12
L5	61·92	Residue	345·7	189·7		—	—	—	—	9·22	32·12	14·62	{0·29 5·67
	288·27				Weights	14·27	13·30	7·49	60·59	123·88	48·04	14·62	6·08
					Per cent. Esters	4·9	4·6	2·6	21·0	43·0	16·7	5·1	2·1
					Per cent. Acids	4·9	4·6	2·6	20·9	43·0	16·7	5·1	2·2
	REFRACTIONATIONS FRACTION L2												
L21	13·55	111–116°	253·3	49·0		4·74	2·11	2·55	4·15	—	—	—	—
L22	14·45	116–117°	259·4	61·7		2·81	2·42	1·63	7·59	—	—	—	—
L23	7·31	117–121°	268·6	75·6		0·24	1·24	—	5·48	0·35	—	—	—
L24	6·52	121–123°	274·2	81·5		—	0·90	—	4·12	1·50	—	—	—
L25	6·11	123–135°	275·8	84·4		—	0·67	—	3·66	1·78	—	—	—
L26	9·48	135°	282·3	87·6		—	0·71	—	3·71	5·06	—	—	—
L27	7·30	Residue	292·3	98·0		—	—	—	1·07	5·95	0·28	—	—
	64·72				Weights	7·79	8·05	4·18	29·78	14·64	0·28	—	—
					Per cent. Esters	12·1	12·4	6·5	46·0	22·6	0·4	—	—

TABLE 107. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF A HYDROGENATED WHALE OIL* (J. T. Terleski)—*continued*

			Refractionations		Calculated Composition of Ester-fractions							
					Saturated		Unsaturated					
No.	G.	Temperature at Head of Flask	S.E.	I.V.	C_{14}	C_{16}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	N–S
			Fraction L3									
L31	11·71	123–130°	276·5	87·0	—	0·95	—	7·02	3·74	—	—	—
L32	9·25	130–131°	279·8	88·8	—	0·58	—	4·54	4·13	—	—	—
L33	8·59	131–133°	282·5	91·4	—	0·29	—	3·63	4·67	—	—	—
L34	10·54	133°	286·9	92·1	—	0·27	—	2·88	7·39	—	—	—
L35	8·73	133–139°	292·2	93·7	—	0·08	—	0·95	7·70	—	—	—
L36	9·35	140–142°	295·3	101·1	—	—	—	0·68	8·00	0·67	—	—
L37	9·69	Residue	303·6	120·7	—	—	—	—	6·55	3·14	—	—
	67·86		Weights		—	2·17	—	19·70	42·18	3·81	—	—
			Per cent. Esters		—	3·2	—	29·0	62·2	5·6	—	—
			Fraction L4									
L41	8·66	134–135°	292·7	94·1	—	0·04	—	0·83	7·79	—	—	—
L42	8·43	135–136°	294·2	96·6	—	—	—	0·59	7·65	0·19	—	—
L43	8·50	136–138°	296·8	97·7	—	—	—	—	8·14	0·36	—	—
L44	8·70	138–140°	298·7	100·5	—	—	—	—	7·64	1·06	—	—
L45	8·74	140°	299·2	102·0	—	—	—	—	7·49	1·25	—	—
L46	10·77	140–144°	302·2	112·3	—	—	—	—	7·90	2·87	—	—
L47	7·22	Residue	317·1*	159·8	—	—	—	—	2·35	4·76	—	0·11
	61·02		Weights		—	0·04	—	1·42	48·96	10·49	—	0·11
			Per cent. Esters		—	0·1	—	2·3	80·2	17·2	—	0·2
			Fraction L5									
L51	8·22	130–144°	305·2	142·3	—	—	—	—	5·03	3·19	—	—
L52	5·99	144–151°	312·9	163·0	—	—	—	—	1·87	4·12	—	—
L53	7·59	151–162°	319·0	181·0	—	—	—	—	0·63	6·96	—	—
L54	6·27	162–164°	327·5	206·9	—	—	—	—	—	4·66	1·61	—
L55	7·24	164–174°	333·9	225·6	—	—	—	—	—	3·54	3·70	—
L56	5·27	174–178°	343·6*	236·9	—	—	—	—	—	1·87	3·30	0·10
L57	5·35	Residue	346·0*	209·8	—	—	—	—	—	1·88	3·33	0·14
	45·93		Weights		—	—	—	—	7·53	26·22	11·94	0·24
			Per cent. Esters		—	—	—	—	16·4	57·1	26·0	0·5

* L47, Esters freed from unsaponifiable matter, S.E. 312·4
* L56, ,, ,, ,, ,, ,, S.E. 337·5
* L57, ,, ,, ,, ,, ,, S.E. 336·5

Equivalents of Saturated Esters present in the Lower Fractions

No.	Saturated Esters, S.E.
L1	249·2
L21	250·0
L22	254·2
L23	265·0

In the above analysis, the unsaponifiable matter was not removed initially, but the primary residual fraction L5 was hydrolysed and the unsaponifiable matter then removed, the recovered acids being re-methylated and refractionated as shown. The 61·92 g. of L5 yielded 5·67 g. of unsaponifiable; in addition, traces of unsaponifiable matter were present in fractions L47, L56, and L57.

The C_{14} and C_{16} unsaturated esters were taken as mono-ethenoid, whilst the remainder were calculated at the following values:

	Mean Unsaturation	S.E.	I.V.
C_{18} unsaturated esters	−2·2H	295·8	94·5
C_{20} „ „	−4·7H	321·3	185·8
C_{22} „ „	−7·1H	346·9	260·0

It will be seen, of course, that the final compositions credited to the primary fractions L2 to L5 are derived from the percentage compositions of the esters determined by refractionation of the respective fractions.

(c) *Calculated Composition of Total Hydrogenated Whale Fat Acids*

Acid	"Solid" Acids (23·1 Per Cent.)	"Liquid" Acids (76·9 Per Cent.)	Total	Fatty Acids (excluding Unsaponifiable) Per Cent. (Wt.)	Fatty Acids (excluding Unsaponifiable) Per Cent. (Mol.)	Mean Unsaturation
Saturated:						
Myristic	4·39	3·76	8·15	8·3	9·9	—
Palmitic	12·37	3·53	15·90	16·2	17·1	—
Stearic	2·72	—	2·72	2·8	2·6	—
Arachidic	0·26	—	0·26	0·3	0·2	—
Unsaturated:						
Tetradecenoic	—	1·98 (−2·0H)	1·98	2·0	2·4	−2·0H
Hexadecenoic	—	16·08 (−2·0H)	16·08	16·3	17·5	−2·0H
Oleic, etc.	1·32 (−2·0H)	33·05 (−2·2H)	34·37	35·0	33·7	−2·2H
C_{20}	1·90 (−2·0H)	12·87 (−4·7H)	14·77	15·0	13·2	−4·4H
C_{22}	0·14 (−2·0H)	3·93 (−7·1H)	4·07	4·1	3·4	−6·9H
Unsaponifiable	—	1·70	1·70	—	—	—

Analytical Characteristics of Hydrogenated Whale Fat (including Unsaponifiable Matter)

	Calculated from Data in (c) (*above*)	Determined on Original Fat
Saponification equivalent	288·5	287·2
Iodine value	86·2	86·6

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TABLE 108. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF AN ANTARCTIC WHALE OIL* (L. Maddison)

In this analysis, the unsaponifiable matter (D) was first removed as far as possible from the mixed soaps (*cf.* p. 466). The mixed acids were then converted into lithium salts and the latter crystallised from 95 per cent. acetone (*cf.* p. 471), leaving in solution lithium salts of the highly unsaturated acid portion (C). The acids from the insoluble lithium salts were resolved by lead-salt separation from alcohol into " solid " (A) and " liquid " (B) acids in the usual way. All esters were distilled through an " E.H.P." column.

The original whale oil had saponification equivalent 287·0, iodine value 108·0. The mixed acids (287·2 g.) from 300 g. of the oil gave the following fractions when submitted to the treatments mentioned above :

	G.	Per cent.	Iodine Value
A Acids from insoluble lead salts, insoluble lithium salts	67·4	23·5	10·7
B Acids from soluble lead salts, insoluble lithium salts	169·0	58·8	105·1
C Acids from soluble lithium salts	48·3	16·8	307·5
D Unsaponifiable matter extracted previously	2·5	0·9	103·6
	287·2		

(a) *Fractional Distillation of Methyl Esters of the Acids A*

(63·53 g. distilled through " E.H.P. column ")

					Calculated Composition of Ester-fractions								
					Saturated				Unsaturated (−2·0H)				
No.	G.	Column Head °C.	S.E.	I.V.	C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	C_{18}	C_{20}	N–S
A1	3·99	95–100	241·8	0·7	3·96	—	—	—	0·03	—	—	—	—
A2	4·69	100–104	243·1	0·5	4·45	0·22	—	—	0·02	—	—	—	—
A3	4·58	104	243·1	0·4	4·33	0·23	—	—	0·02	—	—	—	—
A4	3·34	104–110	252·6	1·2	1·96	1·34	—	—	0·02	0·02	—	—	—
A5	5·28	110–113	265·4	2·8	0·77	4·36	—	—	0·01	0·14	—	—	—
A6	5·59	113–120	267·1	2·9	0·51	4·91	—	—	Trace	0·17	—	—	—
A7	5·73	120	269·3	2·9	0·12	5·43	—	—	—	0·17	0·01	—	—
A8	6·19	120	270·5	4·0	—	5·80	0·12	—	—	0·24	0·03	—	—
A9	5·61	120	271·1	5·8	—	4·95	0·31	—	—	0·31	0·04	—	—
A10	5·52	120	279·3	3·1	—	3·44	1·89	—	—	0·11	0·08	—	—
A11	3·54	120–132	284·5	22·3	—	1·22	1·44	—	—	0·34	0·54	—	—
A12	3·79	132–135	295·4	29·6	—	0·21	2·28	—	—	0·03	1·27	—	—
A13	3·44	135–140	303·2	38·2	—	—	1·50	0·37	—	—	1·14	0·43	—
A14	2·24	Residue	326·4*	68·2	—	—	—	0·29	—	—	—	1·94	0·01
	63·53		Weights		16·10	32·11	7·54	0·66	0·10	1·53	3·11	2·37	0·01
			Per cent. Esters		25·4	50·5	11·9	1·0	0·2	2·4	4·9	3·7	Trace
			Per cent. Acids		25·2	50·5	11·9	1·1	0·2	2·4	4·9	3·8	Trace

* A14, Esters freed from unsaponifiable matter, S.E. 325·2

(*b*) *Fractional Distillation of Methyl Esters of the Acids B*

(166·51 g. distilled through " E.H.P. column ")

					CALCULATED COMPOSITION OF ESTER-FRACTIONS								
		COLUMN HEAD			SATURATED			UNSATURATED					
No.	G.	°C.	S.E.	I.V.	C_{12}	C_{14}	C_{16}	C_{14} (−2·0H)	C_{16} (−2·0H)	C_{18} (−2·4H)	C_{20} (−5·1H)	C_{22} (−8·7H)	N-S
B1	3·80	80–94	237·0	29·3	0·54	2·21	—	1·05	—	—	—	—	—
B2	4·60	94–100	241·6	27·9	—	3·35	0·04	1·21	—	—	—	—	—
B3	4·61	100–102	247·6	39·3	—	2·23	0·62	1·24	0·52	—	—	—	—
B4	4·98	102–104	257·1	63·7	—	0·77	1·00	1·17	2·04	—	—	—	—
B5	4·31	104–110	261·8	67·9	—	0·35	0·94	0·62	2·40	—	—	—	—
B6	6·36	110	266·0	80·6	—	0·13	0·87	0·34	5·02	—	—	—	—
B7	7·29	110	266·5	81·9	—	0·12	0·90	0·32	5·95	—	—	—	—
B8	5·71	110–118	270·2	83·7	—	—	0·69	—	4·58	0·44	—	—	—
B9	7·05	118	278·9	87·9	—	—	0·69	—	3·47	2·89	—	—	—
B10	8·13	118–120	282·0	89·4	—	—	0·72	—	3·14	4·27	—	—	—
B11	10·62	120–125	283·0	90·3	—	—	0·86	—	3·78	5·98	—	—	—
B12	12·93	125–128	285·1	93·9	—	—	0·63	—	4·02	8·28	—	—	—
B13	12·68	128–130	292·7	94·8	—	—	0·70	—	0·55	11·43	—	—	—
B14	12·56	130	293·1	94·9	—	—	0·70	—	0·40	11·46	—	—	—
B15	14·12	130–136	293·8	95·1	—	—	0·77	—	0·10	13·25	—	—	—
B16	13·00	136	295·2	100·7	—	—	—	—	—	13·00	—	—	—
B17	11·79	136	296·5	100·8	—	—	—	—	—	11·34	0·45	—	—
B18	7·26	136–142	309·6	129·2	—	—	—	—	—	3·10	4·16	—	—
B19	5·75	142–155	314·2	171·0	—	—	—	—	—	1·43	4·32	—	—
B20	5·21	155–160	328·1*	236·4	—	—	—	—	—	—	3·59	1·62	—
B21	3·75	Residue	333·0*	167·8	—	—	—	—	—	—	2·48	1·12	0·15
	166·51		Weights		0·54	9·16	10·13	5·95	35·97	86·87	15·00	2·74	0·15
			Per cent. Esters		0·3	5·5	6·1	3·6	21·6	52·2	9·0	1·6	0·1
			Per cent. Acids		0·3	5·5	6·1	3·5	21·5	52·3	9·1	1·6	0·1

* B20, Esters freed from unsaponifiable matter, S.E. 328·0
* B21, ,, ,, ,, ,, ,, S.E. 319·2

	S.E.	I.V.
(C_{18} unsaturated esters taken as	295·6	100·7)
(C_{20} ,, ,, ,,	320·9	203·0)
(C_{22} ,, ,, ,,	345·3	320·0)

TABLE 108. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF AN ANTARCTIC WHALE OIL* (L. Maddison)—*continued*

(c) *Fractional Distillation of Methyl Esters of the Acids C*

(45·74 g. distilled through " E.H.P. column ")

					CALCULATED COMPOSITION ON ESTER-FRACTIONS							
					SATURATED	UNSATURATED						
No.	G.	COLUMN HEAD °C.	S.E.	I.V.	C_{14}	C_{14} (−2·0H)	C_{16} (−2·8H)	C_{18} (−3·3H)	C_{20} (−9·4H)	C_{22} (−10·4H)	C_{24} (−10·4H)	N-S
C1	1·74	80–110	248·4	110·3	0·08	1·09	0·57	—	—	—	—	—
C2	2·18	110	273·6	139·1	—	—	1·63	0·55	—	—	—	—
C3	2·67	110–130	288·0	143·4	—	—	0·60	2·07	—	—	—	—
C4	3·09	130–140	301·5	149·8	—	—	—	2·08	1·01	—	—	—
C5	3·62	140	303·9	192·2	—	—	—	2·04	1·58	—	—	—
C6	4·10	140–145	312·3	330·7	—	—	—	0·76	3·34	—	—	—
C7	4·73	145–150	318·7*	369·3	—	—	—	0·14	4·55	—	—	0·04
C8	4·82	150–160	325·7*	370·2	—	—	—	—	3·86	0·90	—	0·06
C9	4·42	160–164	334·6*	374·3	—	—	—	—	2·97	1·31	—	0·14
C10	4·53	164–170	348·2*	378·0	—	—	—	—	0·78	3·62	—	0·13
C11	4·95	170 falling	346·5*	360·3	—	—	—	—	1·42	3·37	—	0·16
C12	4·89	Residue	376·8*	195·0	—	—	—	—	—	4·04	0·45	0·40
	45·74		Weights		0·08	1·09	2·80	7·64	19·51	13·24	0·45	0·93
			Per cent. Esters		0·2	2·4	6·1	16·7	42·6	29·0	1·0	2·0
			Per cent. Acids		0·2	2·4	6·1	16·6	42·6	29·0	1·0	2·1

	S.E.	I.V.
* C7, Esters freed from unsaponifiable matter,	315·9	370·2
* C8, ,, ,, ,, ,, ,,	321·4	373·4
* C9, ,, ,, ,, ,, ,,	324·4	377·9
* C10, ,, ,, ,, ,, ,,	338·5	381·2
* C11, ,, ,, ,, ,, ,,	335·1	383·4
* C12, ,, ,, ,, ,, ,,	346·2	210·3

	S.E.	I.V.
(C_{16} unsaturated esters taken as	267·2	133·1)
(C_{18} ,, ,, ,,	294·7	142·2)
(C_{20} ,, ,, ,,	316·6	377·1)
(C_{22} ,, ,, ,,	343·6	384·4)
(C_{24} ,, ,, ,,	371·6	355·4)

(d) *Calculated Composition of Total Whale Oil Acids*

Acid	A (23·5 Per Cent.)	B (58·8 Per Cent.)	C (16·8 Per Cent.)	D (0·9 Per Cent.)	Total	Fatty Acids (excluding Unsaponifiable) Per Cent. (Wt.)	Fatty Acids (excluding Unsaponifiable) Per Cent. (Mol.)
Lauric	—	0·19	—	—	0·19	0·2	0·3
Myristic	5·92	3·20	0·03	—	9·15	9·3	11·0
Palmitic	11·88	3·57	—	—	15·45	15·6	16·6
Stearic	2·80	—	—	—	2·80	2·8	2·7
Arachidic	0·25	—	—	—	0·25	0·3	0·2
Unsaturated C_{14}	0·04 (−2·0H)	2·08 (−2·0H)	0·39 (−2·0H)	—	2·51 (−2·0H)	2·5	3·0
,, C_{16}	0·56 (−2·0H)	12·64 (−2·0H)	1·02 (−2·8H)	—	14·22 (−2·1H)	14·4	15·4
,, C_{18}	1·16 (−2·0H)	30·76 (−2·4H)	2·79 (−3·3H)	—	34·71 (−2·5H)	35·2	33·8
,, C_{20}	0·89 (−2·0H)	5·33 (−5·1H)	7·16 (−9·4H)	—	13·38 (−7·2H)	13·6	12·0
,, C_{22}	—	0·98 (−8·7H)	4·88 (−10·4H)	—	5·86 (−10·1H)	5·9	4·9
,, C_{24}	—	—	0·17 (−10·4H)	—	0·17 (−10·4H)	0·2	0·1
Unsaponifiable	Trace	0·05	0·36	0·90	1·31	—	—

Analytical Characteristics of Original Whale Oil (including Unsaponifiable Matter)

	Calculated from Data in (*d*) (*above*)	Determined on Original Fat
Saponification equivalent	286·9	287·0
Iodine value	115·1	108·0

TABLE 109. *COMPLETE FRACTIONATION DATA FOR THE COMPONENT ACIDS OF CEYLON RUBBER SEED OIL* (F. D. GUNSTONE)

In this analysis the mixed fatty acids were first crystallised from acetone (5 c.c. per g.) at −30° C., the filtrates being then cooled to −50° C. The acids left in solution at −50° C. are fraction D. The combined crystals separated at −30° and −50° C. were recrystallised from acetone (5 c.c. per g.) at −30° C., the soluble acids being fraction C. The acids insoluble in acetone at −30° C. were crystallised from ether (10 c.c. per g.) at −30° C., giving a soluble fraction (B) and an insoluble fraction (A).

The original rubber seed oil had saponification equivalent 292·3, iodine value 139·8. The mixed acids (225·5 g.) from 250 g. of the oil gave the following fractions:

	G.	Per cent.	Iodine value
A	46·75	20·7	32·9
B	49·40	21·9	136·2
C	53·98	23·9	178·6
D	75·40	33·5	192·0
	225·53		

The mixed acids of each mixed acid fraction were analysed spectrographically after alkali isomerisation by the method of Hilditch, Morton, and Riley,[28] from which the proportions of saturated, oleic, linoleic, and linolenic acids in each were determined.

Spectrographic Analyses of Mixed Acids A, B, C, D

	$E^{1\%}_{1\,\text{cm.}}$		COMPONENT ACIDS			
	268 mμ *	234 mμ *	SATD.	OLEIC	LINOLEIC	LINOLENIC
A	14·8	90·8	77·5	11·4	8·3	2·8
B	71·5	361·3	8·2	47·0	31·4	13·4
C	151·6	604·3	9·4	13·3	48·8	28·5
D	208·7	628·2	12·4	3·7	44·7	39·2

* $E^{1\%}_{1\,\text{cm.}}$ at 268 mμ after alkali-isomerisation at 170° C. for 15 minutes (pure linolenic acid, 532).

* $E^{1\%}_{1\,\text{cm.}}$ at 234 mμ after alkali-isomerisation at 180° C. for 60 minutes (pure linoleic acid, 906).

Determination of individual saturated acids.—Small proportions of palmitic and stearic acids pass into the mixed acid groups B, C, and D, but the quantity of unsaturated C_{18} acids present in these is so great that accurate determination of the palmitic and stearic acids in the individual fractions obtained by ester fractionation from each group is very difficult. The following procedure was therefore adopted.

(*a*) The mixed acids (A) were converted to methyl esters which were fractionated in the usual way, the results giving the proportions of saturated acids in this fraction.

(*a*) *Fractional Distillation of Methyl Esters of the Acids A*
(37·69 g. distilled through " E.H.P. column ")

					CALCULATED COMPOSITION OF ESTER-FRACTIONS				
					SATURATED			UNSATURATED	
No.	G.	COLUMN HEAD °C.	S.E.	I.V.	C_{16}	C_{18}	C_{20}	C_{18}	N–S
A1	4·00	110–122	273·8	6·8	3·43	0·37	—	0·20	—
A2	9·48	122–118	274·3	12·1	7·75	0·91	—	0·82	—
A3	6·63	118–122	287·1	47·3	2·16	2·22	—	2·25	—
A4	5·37	122–128	296·1	58·5	0·20	2·91	—	2·26	—
A5	4·43	128–126	295·4	45·2	0·23	2·76	—	1·44	—
A6	4·70	120 falling	296·7	29·9	0·10	3·59	—	1·01	—
A7	3·08	Residue	315·4*	18·5	—	0·84	1·84	0·39	0·01
	37·69	Weights			13·87	13·60	1·84	8·37	0·01
		Per cent. Esters			36·8	36·1	4·9	22·2	Trace
		Per cent. Acids			36·7	36·2	4·9	22·2	Trace

* A7, Esters freed from unsaponifiable matter, S.E. 314·3, I.V. 17·5.

TABLE 109—*continued*

(*b*) A separate specimen of the total mixed acids from the original rubber seed oil (120 g.) was converted into methyl esters, which were hydrogenated at 100° with Raney nickel catalyst until action had practically ceased (iodine value 8·3). The hydrogenated mixed esters were then fractionated.

(*b*) *Fractional Distillation of Hydrogenated Mixed Methyl Esters*

No.	G.	COLUMN HEAD °C	S.E.	I.V.	CALCULATED COMPOSITION OF ESTER-FRACTIONS C_{16}	C_{18}	C_{20}	N-S
H1	3·23	–133	275·3	3·6	2·57	0·66	—	—
H2	3·41	133–135	282·7	4·4	1·78	1·63	—	—
H3	3·33	135–130	287·4	5·5	1·18	2·15	—	—
H4	4·00	130–137	290·7	6·7	0·97	3·03	—	—
H5	5·27	137–133	293·6	7·2	0·76	4·51	—	—
H6	6·32	137–135	296·0	7·1	0·41	5·91	—	—
H7	8·24	135–138	296·2	7·3	0·48	7·76	—	—
H8	15·30	138–142	297·1	6·3	—	15·30	—	—
H9	17·92	142–145	296·2	5·0	—	17·92	—	—
H10	4·81	145	297·6	4·9	—	4·81	—	—
H11	1·84	140 falling	296·8	4·7	—	1·84	—	—
H12	3·84	Residue	356·3*	44·0	—	0·91	2·52	0·41
	77·51		Weights		8·15	66·43	2·52	0·41
			Per cent. Esters		10·5	85·7	3·3	0·5
			Per cent. Acids		10·5	85·7	3·3	0·5

* H12, Esters freed from unsaponifiable matter, S.E. 318·1.

The percentages of acids in the above analysis require a minor correction (since the stearic acid in the hydrogenated esters represents original C_{18} acids with a mean equivalent of 280·3 (from the iodine value of the C_{18} acids as calculated from the spectrographic analyses) instead of 284·0). Analysis (*b*) then indicates the total *palmitic* acid+the *unsaponifiable* content of the original oil, whilst the *arachidic* acid content is obtained from analysis (*a*). The final composition of Ceylon rubber seed oil fatty acids is then arrived at as in (*c*).

(*c*) *Calculated Composition of Total Ceylon Rubber Seed Oil Acids*

ACID	A (20·7 PER CENT.)	B (21·9 PER CENT.)	C (23·9 PER CENT.)	D (33·5 PER CENT.)	TOTAL	FATTY ACIDS (EXCLUDING UNSAPONIFIABLE) PER CENT. (WT.)	PER CENT. MOL.)
Unsaponifiable	—	1·80	2·25	4·16	0·50	—	—
Palmitic	7·57				10·60	10·7	11·6
Stearic	7·46				12·15	12·2	11·9
Arachidic	1·01				1·00	1·0	0·9
Oleic	2·36	10·29	3·18	1·24	17·07	17·1	16·9
Linoleic	1·72	6·88	11·66	14·97	35·23	35·4	35·1
Linolenic	0·58	2·93	6·81	13·13	23·45	23·6	23·6

Analytical Characteristics of Original Ceylon Rubber Seed Oil (*including Unsaponifiable Matter*)

	CALCULATED FROM DATA IN (*c*) (*above*)	DETERMINED ON ORIGINAL FAT
Saponification equivalent	292·0	292·3
Iodine value	137·4	139·8

order to convert all unsaturated esters into acidic products (one oxidation is usually insufficient if the iodine value of the original ester exceeds 30–35). (The oxidation can be made more complete in one operation by employing 20 volumes of acetone and an amount of permanganate equal to 10 times the weight of the ester-fraction, in place of the usual 10 volumes of acetone and permanganate equal to 4 times the weight of ester-fraction.) The last traces of acidic products of oxidation are difficult to remove from the saturated esters, and it has been found desirable, when determining the saponification equivalent of the recovered saturated esters, to neutralise the slight remaining acidity with 0·1*N* alcoholic potassium hydroxide before adding the known amount of 0·5*N* alcoholic potassium hydroxide for the actual saponification.

Owing to separation of salts of the acidic products of oxidation over the surfaces of the permanganate crystals, much of the latter remains unused even when it is in a very finely powdered condition. In order to lessen the quantity of inorganic matter which has to be removed from the oxidised material, Steger and van Loon[30] have employed the apparatus shown in Fig. 11. A glass extraction thimble with a sintered base is supported in the funnel which is fitted at its base into the flask, and is connected at the top with a reflux condenser. The glass extraction thimble is filled with permanganate crystals, the acetone solution of the ester is boiled in the flask, and acetone condenses and becomes saturated with potassium permanganate before it falls back into the flask. When reaction ceases, the acetone is distilled and the residue treated with sulphur dioxide solution to reduce manganic oxides. The aqueous solution is extracted with light petroleum, and the latter extract is then washed, first with water to remove mineral acid, and then three times with a 50 per cent. aqueous-alcoholic solution of ammonia or caustic potash to remove acidic products of oxidation. After washing free from alkali with more 50 per cent. aqueous alcohol, the light petroleum solution of the saturated (unoxidised) ester is dried and the latter recovered and weighed. As in the preceding method, more than one oxidation is usually necessary before all of the unsaturated components have been oxidised, and the weight of the unoxidised material does not diminish further on repetition of the process.

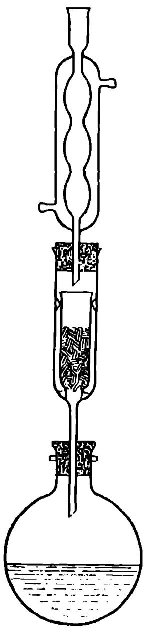

FIG. 11.

When, in the decolorisation of the residual manganic oxides, the solutions are boiled with sodium bisulphite solution, a loss of saturated compounds may occur if myristic and palmitic esters are present, due to the slight volatility of the latter in steam. The weights of higher saturated esters (stearic, arachidic, etc.) obtained agree closely, however, with those demanded by the equivalents and iodine values; whilst, if decolorisation be effected by pouring the acetone solution (after the oxidation is complete) into excess of an ice-cold aqueous solution of sulphur dioxide (containing a little dilute sulphuric acid), beneath a layer of ether, the yields of saturated esters of lower molecular weight are also in close accordance with those deduced from the equivalents and iodine values. As a rule, the equivalent of the saturated esters may be used alone, since this will tend in general to be more accurate than the determination of their weight,[31] but for special cases in which it may be desirable to calculate an ester-fraction in terms of a five-component mixture, the proportion of saturated esters may also be utilised, providing that possible loss of yield has been guarded against by the precautions indicated.

It has been found that, in the esters of " solid " acids from hydrogenated fats, the equivalents of the saturated esters present lie very close (within 1–2 units) to those of the whole ester-fraction (*cf.*, e.g. Table 107, fractions S7, S8, L1, L21, L23). In other words, the saturated and unsaturated components of a final ester-fraction in the analyses conducted as described above possess almost the same mean equivalents. Little alteration in the ultimate component acid figures is, indeed, introduced if the results are calculated throughout on this basis.

It remains to be added that, when it is known that a portion of the ester-fraction will be required for oxidation, it is desirable to collect more (e.g. 7–10 g.) than would otherwise be included in a single fraction, in order to ensure that sufficient saturated ester is present to permit an accurate determination of its saponification equivalent; this applies especially to lower-boiling fractions of esters of "liquid" or mainly unsaturated acids (*cf.* p. 495, Table 107 (*b*), fractions L1, L21, etc.).

Details of the method of calculation involved.* As already stated, the composition of an ester-fraction which, it is reasonably certain, contains esters of only two saturated acids with unsaturated components all of the same carbon content can be deduced from its equivalent and iodine value by comparatively simple calculation as follows:

If a fraction of weight w, equivalent E_w, and iodine value I_w contains a weight u of unsaturated esters (of the same carbon content, e.g. C_{18}) with iodine value I_u and equivalent E_u,

$$u = w . I_w / I_u,$$

and the mean equivalent E_s of the saturated esters $(w-u)$ present follows from the equation

$$E_s = \frac{w-u}{w/E_w - u/E_u}.$$

From E_s the weights of saturated esters are calculated as a binary mixture of the homologues (e.g. C_{16} and C_{18}) between the equivalents of which E_s lies.

Again, ester-fractions which include only (unsaturated) derivatives of acids of two groups in the homologous series (e.g. C_{18} and C_{20}, or C_{20} and C_{22}) can be evaluated directly from their saponification equivalents. In other cases, however, the computation becomes somewhat more complicated, since the weights of more than three independent components are involved.

If x, y, z be the respective weights of saturated and two unsaturated esters in a fraction of weight w, and E_x, E_y, E_z, E_w be the corresponding equivalents and I_y, I_z, I_w be the corresponding iodine values, we have:

$$\begin{aligned} &\text{(i)}\ x+y+z=w \\ &\text{(ii)}\ x/E_x+y/E_y+z/E_z=w/E_w \\ &\text{(iii)}\ y.I_y+z.I_z=w.I_w \end{aligned}$$

(Obviously, in equation (ii), saponification values V_x, V_y, V_z, V_w can be alternatively used if desired, the equation becoming: $x.V_x+y.V_y+z.V_z=w.V_w$.)

The values of y and z, the unsaturated components, are thus determined whilst, from that of x, the binary mixture of saturated esters is evaluated directly from its equivalent (E_x).

Occasionally, in the "liquid" ester-fractions (e.g. pp. 495, 496, Table 107 (*b*), fractions L27, L36, L42), at the point when palmitate and hexadecenoate have almost disappeared and when C_{20} unsaturated esters are beginning to appear, the above equations yield negative values for one or other component when calculated to palmitic, hexadecenoic, and C_{18} unsaturated esters, or to palmitic, C_{18}, and C_{20} unsaturated esters, but give positive values for mixtures of C_{18} unsaturated accompanied by small proportions of hexadecenoate and C_{20} unsaturated esters. In these instances the components may be calculated from the following equations (p, q, r = respectively, C_{16}, C_{18}, C_{20} unsaturated esters in Table 107 (*b*). See also p. 497):

$$\begin{aligned} &p+q+r=w \\ &p/268+q/295{\cdot}8+r/321{\cdot}3=w/E_w \\ &94{\cdot}8p+94{\cdot}5q+185{\cdot}8r=w.I_w \end{aligned}$$

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* An exhaustive mathematical analysis of data and calculations involved in determining the component acids of marine animal oils has been given by Charnley.[31]

It may be pointed out that, in use, the equations (i), (ii), (iii) can be conveniently simplified by employing, in equation (ii), the reciprocal of the equivalents $\times 10^6$. This is best illustrated by a definite example, e.g. Table 107 (*b*), fraction L25 (6·11 g., S.E. 275·8, I.V. 84·4, containing methyl esters of palmitic, hexadecenoic and C_{18} unsaturated esters of S.E. 295·8, I.V. 94·5):

If p, h, and o represent the three classes of esters, the equations are:

$$p+h+o=6{\cdot}11 \tag{i}$$

$$p/270+h/268+o/295{\cdot}8=6{\cdot}11/275{\cdot}8 \tag{ii}$$

$$94{\cdot}8h+94{\cdot}5o=6{\cdot}11\times 84{\cdot}4 \tag{iii}$$

Taking reciprocals $\times 10^6$ in (ii),

$$3704p+3731h+3381o=6{\cdot}11\times 3626$$

Multiplying (i) by 3704,

$$3704p+3704h+3704o=6{\cdot}11\times 3704$$

Subtracting

$$27h-323o=-6{\cdot}11\times 78 \tag{iv}$$

$$94{\cdot}8h+94{\cdot}5o=\ 6{\cdot}11\times 84{\cdot}4 \tag{iii}$$

Eliminating h between (iii) and (iv),

$$2560h-30610o=-6{\cdot}11\times 7394$$

$$2560h+2552o=\ 6{\cdot}11\times 2279$$

$$33162o=6{\cdot}11\times 9673$$

$$o=1{\cdot}78 \text{ g.}$$

(whence $h=3{\cdot}66$ g. and $p=0{\cdot}67$ g.)

The mode of evaluation of the ester-fractionation data in any given case must be considered in relation to the particular circumstances, and choice made accordingly. In the majority of analyses, when the more efficient type of fractionating column has been used, it is rarely found necessary to isolate, and to determine the equivalent of, the saturated components of an ester-fraction. It is difficult to give explicit suggestions to cover all possible cases, but the following illustrative procedures, taken from the data in Tables 105–109, may afford general guidance.

Ester-fractions of the more saturated or "solid" acids. The lead salts of tetra- and hexa-decenoic acids are freely soluble in alcohol, and therefore the small iodine values in fractions of equivalent below about 296 (e.g. Table 106, S1–S13; Table 107, S1–S6) may be attributed solely to methyl oleate, and the calculation is straightforward. This has been the method used when "solid" esters have been distilled with a "Willstätter" flask.

When the "E.H.P. column" is employed, however, it is evident that traces of these acids are detectable in the C_{14} and C_{16} ester-fractions (*cf.* Table 105, S2–S6; Table 108, A1–A11). In such cases it may be assumed that, to a close approximation, the saturated and unsaturated portions of the fraction have the same equivalent, and the calculation may be illustrated with reference to fraction A10, Table 108 (p. 498).

*Whale oil fraction A*10, *5·52 g., S.E.* 279·3, *I.V.* 3·1. (Methyl esters of palmitic (p), stearic (s), hexadecenoic (h), and oleic (o) acids.)

Of the *total* unsaturated esters, from the equivalents, we have:

$$\frac{\%\ \text{hexadecenoate}}{268}+\frac{\%\ \text{oleate}}{296}=\frac{100}{279{\cdot}3}$$

Whence

$$151h=202o$$

From iodine values,

$$94{\cdot}8h+85{\cdot}8o=3{\cdot}1\times 5{\cdot}52$$

Or,

$$\left(94{\cdot}8\times\frac{202}{151}+85{\cdot}8\right)o=3{\cdot}1\times 5{\cdot}52$$

Whence $o=0{\cdot}08$ g. and $h=0{\cdot}11$ g.

So that saturated esters $=5{\cdot}52-0{\cdot}19=5{\cdot}33$ g. at S.E. 279·3,

and $p=3{\cdot}44$ g. and $s=1{\cdot}89$ g.

In marine animal oils in which gadoleic as well as oleic acid is present, the highest "solid" ester-fractions (e.g. A13, A14, Table 108) contain fairly large amounts of these unsaturated esters with some stearate and arachidate, and the foregoing calculation may again be applied.

In instances in which the saturated esters of a fraction have been isolated and their equivalent determined (e.g. Table 107, S7–S9), however, the general equations on p. 505 may be used, with x as the weight of saturated esters of determined equivalent E_x; x is then calculated from its determined equivalent E_x as a binary mixture of saturated esters.

Ester-fractions of the more unsaturated or "liquid" acids. Here again different cases have to be considered.

(a) *Fractions with equivalents below those of unsaturated C_{18} esters.* This portion of the esters includes a certain amount of palmitate and increasing amounts of myristate and any lower saturated esters. In addition, tetra- and hexa-decenoates may be present in small proportions in most vegetable and land animal fats, and more prominently in marine animal fats.

The saturated esters present in these fractions may be isolated (as in Table 107, fractions L1, L21–L23) and the components calculated by the general equations on p. 505, but it is now rarely considered necessary to do this. In practice (using an efficient fractionating column) it suffices to calculate the ester-fractions of equivalent below 270 on the assumption that their saturated and unsaturated parts have the same equivalent (as described above for some of the "solid" esters, e.g. Table 108, A10). This method was used in the cow milk fat esters L3–L8 (Table 105), and the whale oil esters B3–B7 (Table 108).

Ester-fractions with equivalents between 270 and 290 are calculated from the general equations on p. 505 to mixtures of palmitic, hexadecenoic, and unsaturated C_{18} esters (the latter at their observed iodine value and corresponding equivalent). When lead-salt separation has been employed, the presence of stearic acid in the "liquid" acids may be taken as negligible. Instances will be seen in Table 105, L9–L15; Table 106 (b) (i), L4–L7; Table 107, L24–L26, L31–L35, L41; Table 108, B8–B15.

As mentioned below, the observed equivalents of unsaturated C_{18} esters (especially from the more unsaturated vegetable oils) are often about a unit lower than that deduced from their iodine values; the use of the observed equivalents, in calculating the composition of fractions with equivalents between 290 and 294–296, accordingly leads to higher proportions of hexadecenoates being credited than are probably present in these fractions, and it has become the practice of the writer and his colleagues to calculate fractions of S.E. 290–296 arbitrarily from the iodine value alone as mixtures of palmitate and unsaturated C_{18} esters (neglecting hexadecenoate). This is illustrated in the data in Table 105, L10–L16; Table 106 (b) (ii), L8–L10.

(b) *Fractions consisting wholly of unsaturated C_{18} esters.* In vegetable fats and in some land animal fats, unsaturated C_{18} acids are the predominant components and many of the ester-fractions of the more unsaturated ("liquid") acids will consist of these. The following points may be noted in connection with these fractions and their interpretation.

So long as the unsaturated C_{18} ester-fractions consist mainly of oleate, with not more than 10–20 per cent. of linoleate, their determined equivalents accord closely with those deduced from their iodine values. When, however, the ester-fractions contain large proportions of linoleate or linolenate—and this is especially noticeable in liquid seed fats of the "semi-drying " and " drying " oil types—the determined equivalents of unsaturated C_{18} ester-fractions tend to be appreciably lower than those corresponding to the observed iodine values. The cause of this is uncertain, but it is most likely due to the presence of traces of autoxidised esters which may undergo scission during refluxing with alcoholic potash, thereby using perhaps three equivalents of KOH per original fatty ester molecule. However this may be, it should be borne in mind that the determined equivalents of the more unsaturated C_{18} ester-fractions are usually slightly lower than the true figure.

In seed fats in which the unsaturated C_{18} ester-fractions represent the esters of highest molecular weight present, it is of course unnecessary to use the equivalents in the calculations, which depend solely on the iodine value and other means which may be used to allocate the proportions of oleate, linoleate, and linolenate. When, as sometimes happens with the " E.H.P. column," there is a slight progressive separation of oleate and linoleate, each ester-fraction may require independent treatment. In other cases, as exemplified in Table 105, fractions L9–L18, or Table 106 (b) (i), fractions L1–L6, or (b) (ii), L4–L14, the unsaturated C_{18} esters may be treated together and finally resolved (from their mean iodine value) into oleate and linoleate.

In ester-fractions immediately preceding those which consist wholly of unsaturated C_{18} esters there are of course very small proportions of saturated esters. Calculation of the mean equivalent of the latter involves essentially a very small difference between two large numbers, the latter depending respectively upon the equivalent of the unsaturated C_{18} esters (accurately determinable from their iodine value) and upon the determined equivalent of the whole fraction. Slight inaccuracies in the latter cause the deduced equivalents of the small amounts of saturated components to be subject to still greater inaccuracy, and frequently (especially with liquid seed fats) they are very erratic. Consequently, since it is known (when lead-salt separation has been employed) that these saturated esters are almost certainly palmitic, it is better to credit them " as palmitate " than to use their deduced equivalents ; and similarly (when low-temperature crystallisation has been used in preliminary resolution of the mixed acids), it is preferred to credit the saturated esters in fractions preceding those of more or less constant boiling point and maximum iodine value " as palmitate," and those in fractions which clearly consist wholly of C_{18} esters " as stearate."

For the same reason, as already mentioned, allowance for hexadecenoate in ester-fractions from oils of this type which show determined equivalents between 290 and the S.E. of the unsaturated C_{18} esters undoubtedly tends to overestimate hexadecenoic acid, and such fractions are preferably calculated merely " as palmitate " with unsaturated C_{18} esters.

It has already been explained that, when only linoleate and oleate are present, the proportion of each follows directly from the iodine values. When linolenate is also present, each ester-fraction could be separately analysed spectrographically after alkali-isomerisation to conjugated di- and tri-ethenoid acids ; but up to the present it has been considered unnecessary to undertake this multiplicity of operations, and the proportions of the three unsaturated acids have been determined on the mixed acids of each group obtained by the preliminary separation of the total mixed acids (as in Table 109, A, B, C, D, p. 502).

(c) *Fractions with equivalents above those of unsaturated C_{18} esters.* This group is encountered chiefly in fats from aquatic sources (e.g. Table 107, L37, L43–L47, L51–L57 ; Table 108, B17–B21, C4–C12), but also to a small degree in the unsaturated esters from land animal fats (e.g. Table 105, L18 ;

Table 106 (b) (i), L7–L9, (b) (ii), L13, L14). Saturated esters are absent, and the ester-fractions are calculated to binary mixtures of C_{18} and C_{20}, C_{20} and C_{22}, or C_{22} and C_{24}, esters according to their observed equivalents. It is therefore necessary to ascertain as closely as possible the mean equivalent and iodine value of each homologous group (C_{18}, C_{20}, C_{22}, etc.) of esters present in the distilled esters. Since individual ester-fractions containing only one of these groups (C_{18}, C_{20}, or C_{22}) are not as a rule obtained, this is done by plotting the iodine values against the equivalents of the fractions and therefrom deducing the approximate iodine value of each group, which in turn fixes their mean equivalent. Although the mean iodine value deduced for each group (C_{18}, C_{20}, or C_{22} esters) may not be accurate to more than a few units, the corresponding equivalents will be little affected, since an alteration of 0·1 in saponification equivalent due to alteration in unsaturation requires a difference of 4 units in iodine value. For this reason, and also because (although the experimental error of determination of iodine value is probably less than that of determination of equivalent) any differences in the proportions of individual unsaturated members of any group (C_{18}, C_{20}, or C_{22}) in any of these fractions will have much less effect on the equivalent than on the iodine value, it is preferred to employ the equivalents in the calculations in these particular cases.* Iodine values and equivalents thus deduced in the typical ester-fractionation data in Tables 105–109 will be found respectively at the end of Tables 105 (c), 106 (b) (i) and (ii), 107 (p. 496), 108 (b) and (c).

The small proportions of C_{20} (and perhaps C_{22}) acids found in land animal fats are taken together as mixed C_{20-22} unsaturated methyl esters at S.E. 330·0.

Residual fractions from distillation of esters. In the residual fractions from the highest-boiling distillates, the unsaponifiable matter has of course to be allowed for and the equivalent of the esters present determined and employed in calculating the composition of these particular fractions.

When unsaturated components of a fat have undergone autoxidation prior to or during their component acid analysis, oxidised products pass for the most part into the unsaturated or " liquid " esters, and are ultimately found in the residue from the distillation of the latter. When this occurs, the determined equivalent of the fatty acids after removal of the non-fatty (unsaponifiable) matter is of somewhat doubtful accuracy. The presence of oxidised fatty esters is usually indicated by an abrupt fall in the iodine value of the residue as compared with that of the preceding fraction or fractions.

In the case of liquid seed fats, in which small quantities of oxidised fat have thus become concentrated in the residue, it is considered more accurate to employ the calculated equivalent of the unsaturated C_{18} esters as representing that of the esters in the residue. In other instances, in which acids higher than C_{18} are present (e.g. whale oil, Table 108, fractions B21, C12), it is necessary however to rely upon the determined equivalent of the esters freed from unsaponifiable matter.

Further, when a lowered iodine value of the residual ester-fraction indicates oxidation (as in all the examples mentioned), it is considered preferable to take the iodine value of the final distilled ester-fraction as that of the fatty esters in the residue. This has the effect of showing somewhat more unsaturated acids, or acids of higher unsaturation, then were present in the oil when analysed ;

---

* The mean equivalent E_u of esters or acids of the same homologous series of iodine value I_u can be calculated as follows (where E_s is the equivalent of the saturated ester or acid of the same homologous series) :

$$x(12700+I_u)=I_u \times E_s,$$

and
$$E_u=E_s-x$$

but it gives a nearer approximation to the acids present in the original fat in its unoxidised state (*cf.* calculated and observed iodine values of the original whale oil in Table 108 (d), p. 501).

The numerous variants and assumptions suggested in the preceding paragraphs may lend a more uncertain appearance to the analytical procedure described in the above paragraphs than is really the case. Experience in the fractionation technique enables those ester-fractions (e.g. residual fractions, or fractions containing only small amounts of saturated with large proportions of unsaturated C_{18} esters, etc.) in which difficulty of interpretation is likely to be encountered to be made as small as possible. In this way analytical uncertainty can for the most part be confined to fractions which themselves are a very small proportion of the total fatty acids of the fat, and any inaccuracy in an individual ester-fraction has a relatively small effect on the final result. Moreover, each case must be considered to a large extent on its own merits: the mode of preliminary resolution of the total acids should be adjusted to suit the particular combination of fatty acids present; care should be taken to complete the analyses of the more unsaturated portions as rapidly as possible and with minimum exposure to atmospheric oxidation; the ester-fractionation procedure should be conducted so as to give the most suitable range and size of individual fractions, having regard to the fatty esters likely to be present. By attention to precautions of this nature it is generally practicable to obtain component acid data of the order of accuracy indicated below.

Having determined the approximate composition of each fraction, it is a comparatively simple matter to build up the compositions of the "solid" and "liquid" esters as a whole, and therefrom to arrive at that of the whole of the component acids of the original fat. The operations and calculations, in the case of complex fats, are extremely lengthy and tedious, and in these instances a final accuracy, in the higher complex unsaturated acids, of not more than about ±2 units per cent. may be reached. In the numerous natural fats with simpler mixtures of component acids, however, the final figures should be within ±0·5 per cent. of the true values; not infrequently there has been evidence of even closer accordance, but the previous figures represent on the whole a safer general estimate.

Even with the somewhat greater uncertainty attaching to the figures for some of the more highly unsaturated components of fish and allied fats, it may be claimed that the standard of accuracy accessible is not unduly low, especially when compared with that attainable in the quantitative assay of many other natural products of a complexity comparable with that of most natural fats.

In certain instances it has been possible to check the accuracy of the analytical procedure by either of three methods:

(i) *Comparison of the component acids of a hydrogenated fat with those of the original fat.* The mixture of acids from a completely or partially hydrogenated fatty oil is of an essentially different type, so far as the analysis is concerned, from that from the original fatty oil, since the proportion of saturated acids is entirely altered by hydrogenation. A comparison of the results obtained from analyses of original and hydrogenated fats thus affords a somewhat rigorous test of the general accuracy of the procedure. A few instances of the kind, drawn from data in our laboratory records at Liverpool, are given by way of illustration; it is of course necessary to compare the molar percentages of the various homologous acids present in each case.

TABLE 110A

Palm Oil Fatty Acids (*mol. per cent.*) (H. K. Dean)

	Original		After Hydrogenation	
Myristic		1·9		0·7
Palmitic		34·3		35·5
Stearic	5·3		62·7	63·8
Oleic	50·6	63·8	1·1	
Linoleic	7·9			—

Pig Back Fat Fatty Acids (*mol. per cent.*) (W. J. Stainsby)

	Original		Partially Hydrogenated (1)		Partially Hydrogenated (2)	
Myristic		3·5		2·8		2·2
Palmitic		26·6		25·6		28·1
Stearic	14·0		18·1		28·2	
Oleic	41·4	69·0	50·9	69·9	40·5	68·7
Linoleic	13·6		0·9			
C_{20-22} unsaturated		0·9		1·7		1·0

Elasmobranch Liver Oil Fatty Acids (*mol. per cent.*) (A. Houlbrooke)

		Original		After Hydrogenation
C_{14}	Saturated	1·4	1·6	2·5
	Unsaturated	0·2		—
C_{16}	Saturated	15·3	19·4	17·5
	Unsaturated	4·1		—
C_{18}	Saturated	1·4	38·6	39·8
	Unsaturated	37·2		—
C_{20}	Saturated	1·1	16·8	16·8
	Unsaturated	15·7		—
C_{22}	Saturated	—	13·9	13·4
	Unsaturated	13·9		—
C_{24}	Saturated	—	9·7	10·0
	Unsaturated	9·7		—

(ii) *Comparison of component acids from fat-fractions separated by preliminary crystallisation from acetone* (*pp. 520–524*) *with those of the original fat.* Table 110B illustrates typical data for a palm oil and for an ox depot fat.

TABLE 110B

Palm Oil Fatty Acids (*per cent. mol.*) (L. Maddison)

	Fractions from Acetone						
	Least Soluble	Intermediate Fractions			Most Soluble	Total	Analysis of the Original Fat
Percentage of whole fat	7·0	6·8	33·6	10·1	42·5	100·0	—
Component acids (*increments*):							
Myristic	—	—	0·5	0·1	0·6	1·2	0·7
Palmitic	5·4	4·0	16·0	2·9	11·3	39·6	39·8
Stearic	0·2	0·5	1·9	0·3	1·0	3·9	3·6
Hexadecenoic	—	—	1·0	0·1	0·6	1·7	1·5
Oleic	1·4	2·3	13·1	6·0	24·8	47·6	48·2
Linoleic	—	Trace	1·1	0·7	4·2	6·0	6·2

TABLE 110B—*continued*

Ox Depot Fatty Acids (per cent. mol.) (S. Paul)

	Fractions from Acetone				
	Least Soluble	Inter-mediate	Most Soluble	Total	Analysis of the Original Fat
Percentage of whole fat	23·9	40·3	35·8	100·0	
Component acids (increments):					
Lauric	—	0·1	0·1	0·2	0·7
Myristic	0·3	1·0	1·1	2·4	3·2
Palmitic	11·1	12·8	9·5	33·4	32·2
Stearic	7·2	10·0	4·2	21·4	22·6
Arachidic	1·2	0·1	Trace	1·3	—
Tetradecenoic	0·1	0·2	0·3	0·6	0·5
Hexadecenoic	0·3	0·6	1·0	1·9	1·8
Oleic	3·7	15·1	16·4	35·2	37·1
Octadecadienoic	—	0·4	3·1	3·5	1·9
C_{20-22} unsaturated	—	—	0·1	0·1	—

As would be expected, minor component acids present in very small quantities only become detectable in some cases as a result of concentration in one or other of the fractions separated by preliminary crystallisation of the fats from acetone. Similarly, the amount of a minor component acid found by analysis of the mixed fatty acids of the whole fat is frequently slightly lower than that obtained as a result of analysis of the acids from fractions of the fat separated by acetone crystallisation, in one or other of which the minor components usually tend to concentrate.

(iii) *Comparison of component acids in fats, the mixed acids of which have been partially separated either* (a) *by lead-salt separation or* (b) *by low-temperature crystallisation from solvents.* The data in Table 110C give interesting illustrations of the accordance between analyses in which both methods of preliminary resolution of the mixed acids have been employed. The analyses of sunflower seed oil and groundnut oil component acids were carried out with the same specimen of the respective oils; that of sesamé oil was not made on the same sample, although in both analyses the oil came from the same source of supply.

TABLE 110C

Sunflower Seed Oil Component Acids (per cent. wt.)

	A (J. P. Riley)	E (J. P. Riley)	L (Y. A. H. Zaky)	S (J. P. Riley)
Myristic	Trace	0·1	—	
Palmitic	6·4	6·1	5·6	11.1
Stearic	3·2	3·7	2·2	
Arachidic	0·9	0·7	0·9	
Hexadecenoic	0·4	1·1	25·1	21·0
Oleic	21·6	20·8		
Linoleic	67·5	67·5	66·2	67·9

	Groundnut Oil		Sesamé Oil	
	A (J. P. Riley)	L (H. Jasperson)	A (J. P. Riley)	L (M. B. Ichaporia)
Myristic	0·5	—	0·1	—
Palmitic	8·0	8·3	8·2	9·1
Stearic	4·4	3·1	3·6	4·3
Arachidic	6·6	6·6	1·1	0·6
Behenic			—	—
Lignoceric			—	—
Hexadecenoic	1·7	56·0	0·5	45·4
Oleic	52·5		45·3	
Linoleic	26·3	26·0	41·2	40·4

A. Preliminary resolution of mixed acids by low-temperature crystallisation from acetone and ether.

E. Preliminary resolution of mixed esters by low-temperature crystallisation from acetone and ether.

L. Preliminary resolution of mixed acids by lead-salt separation.

S. Analysis of mixed acids by spectrographic method (after alkali isomerisation).[16]

II. Quantitative Investigation of Component Glycerides

(a) QUANTITATIVE DETERMINATION OF FULLY SATURATED GLYCERIDES IN A NATURAL FAT

The method employed (Hilditch and Lea[32]) involves the removal of large amounts of acidic compounds, mainly azelao-glycerides, from the oxidised fat. This process is attended by the production of emulsions, and it is clearly essential to take all precautions to keep the latter at a minimum, and to ensure that removal of the neutral, fully saturated glycerides from the aqueous alkaline solutions of the acidic products is complete. Under the best conditions it is impossible to be sure of the recovery of a minimal amount of fully saturated glycerides, probably of the order of 0·1–0·3 g., which may be left dispersed in the aqueous salt solutions. It is therefore strongly recommended to oxidise sufficient fat to obtain at least 1–2 g., and preferably more, of the fully saturated components.

In practice this means that, for fats of very low fully saturated glyceride content, at least 50 g. and usually 100 g. or more, if available, should be employed. Again, when it is required to determine the component acids of the fully saturated glycerides it is desirable to have at least 20 g. of these, and again, therefore, the oxidation of 50–100 g., or sometimes considerably more, of the fat must be undertaken. The procedure described below is for the oxidation of 100 g. of fat. When larger quantities are to be worked up, it is best to deal with batches of 100 g., or at most 150 g., at a time.

The *neutralised* fat (100 g.) is dissolved in dry acetone (1,000 c.c.) in a 3-litre round-bottomed flask fitted with a long air condenser. The solution is heated nearly to boiling, and then finely powdered (passing a 50-mesh sieve) potassium permanganate (400 g.) is added in small amounts, with vigorous shaking after each addition ; successive additions are made as soon as the solution (which is not heated externally during this part of the process) ceases to boil as a result of the heat evolved by the action of the previous addition. After all the permanganate is added, the contents of the flask are gently refluxed for several hours ; the acetone is then distilled off, the last traces being removed by evacuation (water-pump). The residue is then transferred to a large evaporating basin, ground to a fine powder and well mixed with powdered sodium bisulphite (500 g.). The mixture is cautiously added to water in another basin until the first vigorous action subsides and all unchanged permanganate has been reduced. (Any residual traces of product in the flask are removed by shaking with sodium bisulphite and hot water, and added to the main solution.) To the solution 30 per cent. aqueous sulphuric acid is now added until it is slightly acid to Congo red paper, and heat is then applied until the evolution of sulphur dioxide is completed. The mixture is then boiled until all manganic oxides have disappeared, cooled, and extracted with ether to remove the organic compounds or, if fully saturated glycerides are present in large amount, treated as described below.

SEPARATION OF NEUTRAL (FULLY SATURATED) GLYCERIDES FROM ACIDIC OXIDATION PRODUCTS

(*a*) When the proportion of fully saturated glycerides is fairly large, it is best to remove the solid layer of organic matter which solidifies on top of the cooled aqueous mineral acid extract, to wash this free from traces of mineral acid and salts by heating with water two or three times, and finally to dissolve the washed, solid fat in ether (10 vols.) and cool the solution for some hours at 0°. Fully saturated glycerides which then separate are filtered, washed with cold ether, and, if necessary, united for further purification with the fully saturated glycerides removed from the ether filtrates, etc. (see below).

The original aqueous mineral acid extract is united with the aqueous wash-liquors from the solid layer of fat, and is extracted with ether. This extract is united with the ether filtrates (from the crystallised fully saturated glycerides) for removal of acidic products of oxidation as described below.

(*b*) If the amount of fully saturated glycerides is small, the above division into ether-insoluble and ether-soluble matter may be omitted. In this case the whole of the cooled aqueous mineral acid liquor is, as mentioned above, extracted thoroughly with ether, and the ether extract is washed with water to free it from mineral acid.

The removal of acidic oxidation products from the ether solutions is the most difficult part of the process, on account of the great tendency of the alkali salts of azelao-glycerides to promote the formation of emulsions. The procedure is different according to the proportion of mono-azelao-glyderides (i.e. mono-oleo-glycerides in the original fat) which may be present.

(i) *When the proportion of mono-azelao-glycerides is unlikely to exceed about 25 per cent. of the whole fat* the ether solution may be cautiously extracted alternately with 10 per cent. aqueous potassium carbonate solution and with distilled water. The separating funnel containing the mixture should not be violently agitated, especially in the earlier stages of removal of acidic matter. The azelao-glyceride alkali derivatives are readily partially hydrolysed by water, and this is one reason for the alternation of alkaline and pure aqueous washings. In addition, however, the alkali salts of the azelao-glycerides are readily soluble in ether (see below) and consequently tend to pass into solution in the ether phase in presence of aqueous alkaline solution.

It is also useful, although not essential, to precede the first washing with potassium carbonate solution by two or three extractions with a 10 per cent. solution of potassium bicarbonate; the latter removes the monobasic acids (nonanoic, hexanoic) formed by oxidation and also a considerable part of the diazelao-glycerides, with less tendency to emulsification, but leaves the mono-azelao-glycerides almost entirely in the ether layer.[33]

When the greater part of the acidic products have been removed in the course of the main potassium carbonate and water washings, the agitation should be made more thorough in order to effect complete neutralisation and removal of all acidic compounds. When no further material is removed by alkali, the ether solution is very thoroughly washed with water. All the alkali and aqueous washings are united and re-extracted with ether in order to remove any traces of neutral compounds which may have been dispersed in the aqueous phase by emulsification. The ether is distilled from the united ether extracts and the residual crude fully saturated glycerides are dried by heating at 100° in a vacuum, and weighed. These still retain minor amounts of acidic compounds and, if sufficient in quantity, are further purified as described later (iv).

If they are too small in amount for further purification, the acid value and proportion (if any) of unsaponifiable matter are determined, and the weight is corrected accordingly (in the case of acidic matter, this may be assumed to be, e.g. azelaopalmitostearin, or alternatively, since the average acid value of the acidic products present is known to be usually of the order of 120, this figure may be used).

Before, however, the neutral products are accepted as fully saturated glycerides their iodine value must be determined. If this exceeds 1, *the crude product should be re-submitted to the whole oxidation process.* In some cases a third oxidation may be necessary before all unsaturated and semi-oxidised neutral glycerides have been completely converted into acidic compounds. If the fat under investigation possesses an iodine value of more than 25–30, complete oxidation is rarely effected in one operation.

(ii) *When the proportion of mono-azelao-glycerides is fairly large* a considerable amount of these may be separated, as sodium or potassium salts, by deposition from the ether solution. In this case, prior to extraction with aqueous potassium bicarbonate or carbonate solution, the ether solution of the oxidation products is first cooled at 0° for several hours (if ether-insoluble glycerides have not already been separated earlier, *cf.* above) in order to eliminate any fully saturated glycerides insoluble in ether at 0°. (These are of course filtered separately and washed with cold ether.) The ether filtrates and washings are then warmed to about 30° and shaken vigorously with a small quantity (50–100 c.c.) of a similarly warm saturated solution of sodium or potassium carbonate. The small amount of aqueous alkali emulsion is rapidly run off after standing for a few moments, and the almost clear ether solution is set aside at 0° for several hours. The sodium (or potassium) salts of the mono-azelao-glycerides are deposited in a crystalline form and can readily be removed by filtration and washing with cold ether. (From the alkali salts the free mono-azelao-glycerides may be obtained by acidification in aqueous solution and extraction with ether; they may be purified subsequently by crystallisation from acetone at 0°.)

The use of sodium carbonate leads to separation of more of the mono-azelao-glycerides than when potassium carbonate is employed; on the other hand, the products isolated in the form of potassium salts are purer than the corresponding material obtained as sodium salts.

The ether filtrates and washings from the above mono-azelao-glyceride separation, together with the separated emulsion of aqueous alkali carbonate solution, are mixed and then submitted to the whole of the aqueous potassium carbonate and water washings described above under (i).

(iii) Steger and van Loon [34] have described *an alternative procedure for removal of the acidic products of oxidation.* The organic compounds are recovered from the decolorised aqueous solution of mineral acids and salts by extraction with light petroleum (b.p. 40–60°), and the acidic products are extracted therefrom with a solution of ammonia in 50 per cent. aqueous alcohol. This removes much of the acidic compounds, but the ammonium salts of some of the latter are partly soluble in the light petroleum. The latter solution is therefore shaken with calcium chloride solution, washed with water, and dried. The light petroleum is then removed by distillation and the residue extracted with ethyl acetate, which dissolves neutral fatty matter but leaves the calcium salts of the acidic products. Evaporation of the ethyl acetate solution yields the fully saturated glycerides free from acidic products.

(iv) When 20 g. or more of crude fully saturated glycerides (obtained as in the above procedures) are available, a *further purification process* may conveniently be applied:

The crude fully saturated glycerides are boiled in an open basin with water to which dilute potassium carbonate is added until the whole just remains definitely alkaline to phenolphthalein. The aqueous layer (which contains some emulsified neutral glycerides) is siphoned from the clear upper layer of neutral fat, and the latter is boiled several times with water until the washings are neutral. By this means 80–90 per cent. of the crude fully saturated glycerides are obtained in the form of material of negligible acid value whilst ether extraction of the united alkaline and aqueous washings yields a further quantity of fully saturated material which possesses a definite, though low, acid value. The free acidic compounds from the extracted aqueous alkaline washings are isolated and their acid value determined, and the latter value is employed as a correcting factor for the acidic impurity in the ether extracted portion. In this way the proportion of fully saturated glycerides present in the original fat can usually be determined with a probable experimental error of less than 1 per cent.

The following numerical data for the oxidation of a butter fat may serve to illustrate the above method of purification:

The fat yielded, as a result of complete oxidation, 33·6 per cent. of crude neutral products; oxidations were conducted on six batches of 100 g. each, in order to provide sufficient material for detailed analysis.

On boiling the crude neutral product with dilute potassium carbonate, as described above, there were obtained :

(*a*) 163·8 g. completely neutral fat, sap. equiv. 229·3 (acid value 0·4)
(*b*) 22·9 g. fat extracted by ether, sap. equiv. 234·1 (acid value 6·4) ;
(*c*) 12·5 g. acidic material, sap. equiv. 167·9 (acid value 211·2).

Assuming that the acidic matter present in (*b*) has the same acid value as (*c*), the proportion of fully saturated glycerides in the original fat is

$$\frac{33\cdot6}{199\cdot2}\left(163\cdot8+\frac{22\cdot9\times204\cdot8}{211\cdot2}\right)=31\cdot4 \text{ per cent.}$$

Further examination of fully saturated glycerides. In isolated cases it has proved possible to identify definite components by fractional crystallisation from ether or acetone. Frequently it has been found useful to effect a rough separation into groups of component fully saturated glycerides by employing a less drastic crystallisation procedure, with acetone or ether as solvents, of the nature described on pp. 520–524. If the quantity of the crystallised fractions permits, ester-fractionation of their component acids throws further light on the various forms of mixed saturated triglycerides which may be present.

In the majority of cases, however, the examination has been confined to determination of the component acids of the fully saturated glycerides as a whole ; this nevertheless permits the component acids of the mixed saturated-unsaturated glycerides of the fat to be determined by difference, and in this way gives a certain degree of insight into the structure of the latter, as well as of the fully saturated, types of mixed glyceride present. As an illustration of the kind of data obtainable by combining the determinations of fully saturated glycerides with those of component fatty acids, the figures for a hydrogenated sesamé oil are quoted in Table 111.

TABLE 111. *COMPONENT ACIDS OF THE FULLY SATURATED AND MIXED SATURATED-UNSATURATED ACIDS OF HYDROGENATED SESAMÉ OIL, I.V.* 27·7 (M. B. Ichaporia)

Fully saturated glycerides : 32·4 per cent. (wt.) or 32·7 per cent. (mol.).

	WHOLE FAT COMPONENT ACIDS		FULLY SATURATED GLYCERIDES COMPONENT ACIDS	
	PER CENT. (WT.)	PER CENT. (MOL.)	PER CENT. (WT.)	PER CENT. (MOL.)
Palmitic	9·0	9·9	14·8	16·2
Stearic	59·6	58·9	83·5	82·3
Arachidic	1·0	0·9	1·7	1·5
Oleic (and *iso*-oleic)	30·4	30·3	—	—

Distribution of Acids in the Component Glycerides of the Fat

	WHOLE FAT	FULLY SATURATED GLYCERIDES	MIXED SATURATED-UNSATURATED GLYCERIDES (BY DIFFERENCE)
	100 MOLS.	32·7 MOLS.	67·3 MOLS.
Palmitic	9·9	5·3	4·6
Stearic	58·9	26·9	32·0
Arachidic	0·9	0·5	0·4
Oleic (and *iso*-oleic)	30·3	—	30·3

(b) QUANTITATIVE DETERMINATION OF TRI-C_{18} GLYCERIDES BY MEANS OF HYDROGENATION

It has been stated in several places in the present book that, in many instances, tri-C_{18} glycerides present (usually as oleo- and/or linoleo-glycerides) in fats may be estimated (*a*) by converting the fat or fat-fraction into a totally saturated mixture by hydrogenation, and estimating the tristearin in the product, or (*b*) by partial hydrogenation to varying stages, determination of the amount and composition of the fully saturated glycerides at each stage, and therefrom the composition of the mixed saturated-unsaturated glycerides as above (*cf.* e.g. Chapter VI, pp. 238–240). This is a procedure which should be used with caution, and indeed avoided where possible. It has proved of considerable use in the earlier stages of the study of glyceride composition, but the subsequent advances in preliminary resolution of mixed glycerides by crystallisation have made its employment less necessary. The objections to its use are twofold:

(i) It has been found [35] that a small but definite amount of acyl migration occurs during hydrogenation of fats at 180° C. or above; the process is slow, but might affect the results in the case of prolonged hydrogenation at 180°, since some tristearin, for example, might by acyl interchange become converted into palmitodistearin, etc. The danger of acyl migration can, however, be overcome by conducting the hydrogenation below 100° (e.g. with Raney nickel catalyst, *cf.* below).

(ii) The determination of tristearin in a mixture of tristearin and palmitodistearin (*cf.* below) from saponification equivalent is unsatisfactory, since the small difference of 9·3 units between the equivalents of the two glycerides demands extremely accurate determination of equivalents. Moreover, for some reason at present unknown the determined equivalents of glyceride fractions recovered from ether not infrequently tend to be fractionally lower (0·3–0·5 units) than their true value.

The use of the equivalent alone in the determination of tristearin could be avoided by preliminary resolution of a completely hydrogenated fat from acetone into two or three fractions, and determination of the palmitic and stearic acids in each by the more tedious method of ester-fractionation. The acetone crystallisation should ensure that tristearin is present only with palmitodistearin in the portion least soluble in acetone.

A few practical notes are given here in connection with the hydrogenation process and with the determination of tristearin in completely hydrogenated fats:

Hydrogenation. Any of the well-known methods of hydrogenation in the liquid phase may of course be employed, with either platinum, palladium or nickel as catalyst. The latter is probably most convenient since, in work of this nature, quantities of from 50 up to 400 g. of hydrogenated fat may be required. For hydrogenation below 100° C. the use of Raney nickel catalyst is recommended; but it is usually desirable to complete the process with nickel-kieselguhr catalyst at 130–140° C. for a short period.

Catalyst preparation. (*a*) *Raney nickel catalyst.*[36] Nickel-aluminium alloy (50 per cent. Ni, 50 per cent. Al) is ground so as to pass through an 80-mesh sieve; the powdered alloy (10 g.) is slowly added (during 2 hours) to an ice-cold solution of sodium hydroxide (10 g.) in water (40 c.c.), with occasional stirring. The mixture is then heated in an oil bath at 120° C. for 2 hours, after which 13 c.c. of 20 per cent. sodium hydroxide solution is added, and the mixture kept stirred at 120° C. for 3 hours more, adding distilled water as requisite to replace loss by evaporation. The solution is cooled, diluted to 100 c.c., and the clear layer of sodium aluminate solution then poured off, and the nickel washed carefully with distilled water into a beaker, leaving behind any lumps of solid aluminate. The nickel is washed ten times by decantation with warm distilled water, and then transferred to a Buchner funnel and washed several times with alcohol (taking care not to allow the filter cake to be exposed to air). Finally the nickel is washed with alcohol into a small stoppered bottle and stored under 100 c.c. of alcohol. It is advisable not to store the nickel for any length of time before use.

(*b*) *Nickel-kieselguhr catalyst.* The catalyst may be prepared by dissolving crystalline nickel sulphate (125 g.) in water (1,000–1,500 c.c.) and adding kieselguhr (70 g.) of good quality. The suspension of kieselguhr in the nickel sulphate solution is boiled whilst anhydrous sodium carbonate (125 g.) is gradually added with vigorous stirring. After the addition of the carbonate is completed, the mixture is boiled freely for a few minutes, filtered at the pump, and the solid residue well washed with hot water. The washed cake is transferred to a basin, boiled with water, refiltered and washed, and this process is repeated until the washings are entirely free from carbonate and sulphate. The cake is then dried at 100° and passed through a 50-mesh sieve. It is conveniently reduced (ca. 40 g. at a time) in a silica tube 3 feet long by 1 inch diameter heated in an ordinary combustion furnace. Reduction should be carried out for 1–1½ hours in a current of electrolytic hydrogen at a temperature of 400–450°. The reduced catalyst is allowed to cool in the current of hydrogen to room temperature, and the hydrogen is then replaced for 20–30 minutes by a current of carbon dioxide. The product may be stored in glass bottles in an atmosphere of carbon dioxide, and can be quickly weighed out on a balance in air as required without appreciable loss of activity.

Process of hydrogenation. The fat to be hydrogenated (50–400 g.), together with 2–5 per cent. of its weight of Raney nickel catalyst, is placed in an iron vessel fitted with a flange, to which the cover is bolted, the joint being rendered gas-tight by means of a gasket. The cover is fitted with inlet and outlet valves, a thermometer pocket and a vertical stirrer passing through a stuffing box. The hydrogen is contained in a small gasometer supplied with gas from a cylinder and is passed through an inlet meter into the hydrogenation vessel. From thence it passes through a Drechsel bottle, containing a little water in order to observe the rate of flow of the hydrogen, to the exit meter. The apparatus is tested for leakage of gas by passing hydrogen through it and noting the readings of the inlet and exit meters. If these are concordant, the passage of hydrogen is continued and the vessel rapidly heated by means of a Bunsen burner, whilst the contents of the vessel are stirred. When the temperature reaches 50° C., the needles of both meters are returned to zero and the difference between the readings of the inlet and exit meters gives the volume of gas absorbed by the oil as the hydrogenation proceeds. The hydrogenation should be conducted at 65° C., or as little above this as is consistent with reasonably rapid absorption of hydrogen, for the greater part of the process. Towards the end the rate slackens off considerably, and it is best then to add a small amount of reduced nickel-kieselguhr catalyst and complete the hydrogenation at 130–140° C. as rapidly as possible. When the requisite amount of hydrogen, calculated from the drop in iodine value required, is absorbed, the valves on the vessel are closed and the stirring stopped, the temperature being allowed to fall to about 100° C. The hydrogenation vessel is then rapidly opened and the catalyst removed by filtration, using a Buchner flask and funnel previously heated in a steam oven in order to maintain the fat in a liquid state during filtration. The vessel and filter are washed with boiling acetone and the fat obtained after complete removal of the solvent added to the main bulk. In the case of full hydrogenation of a fat, the catalyst may become de-activated towards the end of the operation and it then becomes necessary to add a further portion of fresh catalyst in order to complete the hydrogenation.

For quantities of 100 g. (or less) of fat the iron vessel may be replaced conveniently by a three-necked round-bottomed flask of 500 c.c. capacity (or less), the stirrer being fitted through a leak-proof joint in the central neck, and the side necks carrying the inlet and exit gas connections together with a thermometer.

Estimation of tristearin in fully hydrogenated fats. A suitable quantity of the completely hydrogenated fat (e.g. 20–50 g.) is crystallised repeatedly from large volumes of pure ether, either at 0° or room temperature. The proportions of ether and crystallisation temperatures used depend on the relative amounts of, for instance, dipalmitostearin, palmitodistearin, and tristearin present. Usually, an initial crystallisation at 0°, using about 10 c.c. ether per gram of fat, serves to separate nearly all the dipalmitostearin present, together with any traces of semi-hydrogenated fat (mono-oleo-glycerides) and unsaponifiable matter, from the bulk of the palmitodistearin and the whole of any tristearin present, these being deposited as crystalline solids. The products remaining in solution in the ether are recovered and, if in sufficient quantity (i.e. more than about 7 g.), may be again submitted to crystallisation from a more concentrated solution (e.g. 5 c.c. ether per gram of fat) at 0°. The insoluble products from the first separation are further repeatedly crystallised, if necessary first at 0°, but in later cases at room temperature, employing increasing proportions of solvent (up to 20–25 c.c. ether per gram of fat) as the solubility of the deposited glycerides becomes progressively less.

In this way a series of fractions is obtained, on each of which a determination of saponification equivalent is made, and (in the case of the most soluble fractions) determinations of iodine value and of the proportion of unsaponifiable matter (from the equivalents of the mixed acids after removal of the latter). Each fraction is then assumed to contain only two components of the type tristearin-palmitodistearin, palmitodistearin-dipalmitostearin, or dipalmitostearin-tripalmitin. The composition of each fraction is then calculated from its observed equivalent, allowance being made in the most soluble fractions for any unsaponifiable matter and mono-oleo-glycerides. (Saponification equivalents of tristearin 296·7, palmitodistearin 287·3, dipalmitostearin 278·0, tripalmitin 268·7.)

The percentages of the various saturated glycerides are thus obtained, but only that of the *tristearin* (including any minor amount of oleodistearin) is actually used in any subsequent calculation. This is because the procedure (which is not absolutely reliable for tristearin, *cf.* above) does not lend itself to accurate determination of the dipalmitostearin, etc., present in the most soluble fractions. For purposes of calculation, therefore, only the determined *tristearin* content is utilised ; the component acid analysis of the fat or fat-fraction under investigation provides more accurate data for the palmitic, etc., acids present, and, after deducting the tristearin found as *tri-C_{18} glycerides*, the remaining acids of the fat or fat-fraction can usually be allocated as mixtures of palmitodi-C_{18} and dipalmitomono-C_{18} glycerides. (This process, of course, has only been found useful for the many fats in which palmitic, stearic, oleic, and linoleic acids are the only major component acids.)

Some typical results obtained by the ether crystallisation procedure outlined above, for fractions of cacao butter initially obtained by preliminary crystallisation of the fat from acetone, are given in Table 112.

TABLE 112. *FRACTIONAL CRYSTALLISATION OF COMPLETELY HYDROGENATED CACAO BUTTER FRACTIONS* (W. J. Stainsby)

From completely hydrogenated fraction A
(*least soluble*, 86·5 *g.*, *I.V.* 0·2)

No.	G.	M.P.	Sap. Equiv.	Iod. Val.
A	40·0	72·0°	296·8	—
B	9·4	69·0°	294·0	—
C	14·2	69·0°	294·4	—
D	7·7	67·0°	291·7	—
E	8·9	65·0°	290·0	—
F	6·3	—	301·8*	1·8
From completely hydrogenated fraction B (*intermediate*, 84·1 *g.*, *I.V.* 0·5)				
A	12·3	70·0°	292·3	—
B	11·1	67·5°	289·1	—
C	7·6	67·5°	288·5	—
D	10·3	66·5°	287·9	—
E	4·6	65·5°	285·3	—
F	11·6	65·5°	285·4	—
G	8·0	65·0°	285·6	—
H	9·4	64·5°	284·8	0·7
I	9·2	—	290·0*	2·3

TABLE 112. *FRACTIONAL CRYSTALLISATION OF COMPLETELY HYDROGENATED CACAO BUTTER FRACTIONS* (W. J. Stainsby)—*continued*

From completely hydrogenated fraction C
(most soluble, 81·1 *g.*, *I.V.* 1·0)

A	11·1	71·0°	295·9	—
B	8·6	68·5°	291·4	—
C	8·7	66·0°	289·4	—
D	13·5	65·0°	287·8	—
E	11·5	64·0°	283·4	—
F	6·3	63·5°	281·9	—
G	7·6	62·5°	282·8	0·8
H	13·8	—	307·6*	4·6

* Sap. equiv. (after removal of unsaponifiable matter) respectively 288·4 (*A*), 285·0 (*B*), 284·6 (*C*).

Estimated composition (mol. per cent.) of completely hydrogenated fractions A, B, C
(from tristearin content and component acid analyses)

	A	B	C
Tristearin	73·0	12·1	20·2
Palmitodistearin	27·0	78·9	60·9
Dipalmitostearin	—	9·0	18·9

(*c*) PRELIMINARY SEPARATION OF A SOLID OR SEMI-SOLID FAT BY CRYSTALLISATION FROM ACETONE

This procedure, which is becoming increasingly useful in studying the glyceride structure of solid or semi-solid fats, results in the concentration of the fully saturated, mono-unsaturated-disaturated, di-unsaturated-monosaturated, or tri-unsaturated glycerides of the fat into groups in which one or other of these types largely predominates. As a result of several systematic crystallisations and recrystallisations from varying proportions of acetone either at 0° or at room temperature, two, three, or more of these groups or fractions of the fat may be obtained. Usually it is possible to effect separation into three groups, the chief components of which in most instances (but not in milk fats or other fats containing a high proportion of fatty acids of lower molecular weight than myristic) will be as follows :

A. *Least soluble :* Fully saturated and mono-unsaturated-disaturated glycerides (with very small proportions, possibly, of di-unsaturated-monosaturated glycerides).

B. *Intermediate :* Mainly mono-unsaturated-disaturated glycerides, but some di-unsaturated-monosaturated glycerides are always present and, sometimes, a small proportion of fully saturated glycerides.

C. *Most soluble :* Tri-unsaturated glycerides and most of the di-unsaturated-monosaturated glycerides ; but a little mono-unsaturated-disaturated glyceride may also be present.

The conditions for optimum separation naturally differ according to the particular fat under investigation. Experience goes to indicate, however, that the best method is first of all to crystallise the fat from anhydrous acetone (5–10 c.c. per gram of fat) at 0°, leaving the solution to stand at 0° for three or four days. This ensures maximum deposition of the mono-unsaturated glycerides, the last portions of which seem to separate very slowly. The soluble portion then consists almost wholly of di- and tri-unsaturated glycerides and may be dealt with separately. The insoluble portion is again dissolved in acetone, this time in somewhat more concentrated solution (e.g. 3–5 c.c. per gram of fat) and left to crystallise overnight at room temperature. This usually results in the deposition of a crop of iodine value not exceeding 25 (and sometimes much less), which may be considered sufficiently free from di-unsaturated glycerides for the purpose of study, or, if not, may be submitted to a repetition of the last-mentioned process.

The part soluble in acetone (from the crystallisation at room temperature) may with advantage again be crystallised from acetone (5–10 c.c. per gram of the portion, according to circumstances) at 0° for 3 or 4 days, when a crop (referred to above as "intermediate") is usually obtained which contains a very high proportion of mono-unsaturated-disaturated glycerides (with possibly some fully saturated glycerides). The (usually relatively small) portion left in solution at this stage consists largely of di-unsaturated glycerides, but its iodine value is usually several units lower than that of the main "most soluble" group obtained in the primary crystallisation. A further crystallisation of this small fraction (which should only amount to 5 per cent. or so of the original fat) under the same conditions as in the preceding instance may give a further separation into two sub-fractions which, though not quite as low or high in iodine value, respectively, as the main "intermediate" and "most soluble" groups, may usually be added respectively to these without serious detriment to their further detailed investigation.

The above outline is, of course, largely illustrative and each fat must be dealt with as its composition demands. If a large quantity of fat is to be studied, a preliminary series of crystallisations on a portion of it (e.g. 100–300 g.) will serve to point to the most suitable procedure for the bulk. The following points, however, appear to be generally applicable:

(i) Anhydrous acetone should be employed, and any acetone recovered from a previous crystallisation should be carefully redistilled over calcium chloride before further use. The presence of very little moisture in acetone has a pronounced effect on the solubility therein, especially at 0°, of the di-unsaturated-monosaturated glycerides.

(ii) The mono-unsaturated-disaturated glycerides separate more completely, as a rule, from acetone in dilute than in concentrated solution. This seeming paradox is not quite correctly stated, of course; what is really meant is that, in a more concentrated solution, the concentration of the di-unsaturated glycerides present is also higher, and the problem is really the separation of the mono-unsaturated-disaturated and fully saturated glycerides from a *mixed solvent* which consists of acetone plus the dissolved di-unsaturated glycerides. The solubility of the mono-unsaturated and fully saturated groups increases markedly with increase in the concentration of di-unsaturated glycerides in the acetone.

(iii) To obtain a minimum amount of mono-unsaturated-disaturated glycerides in the "most soluble" group, the acetone solutions should be left at 0° for at least three days.

Three instances of the application of this preliminary separation of the mixed glycerides in natural fats are given below (Table 113). In the first two of these (ox depot and cow milk fats) the initial procedure (primary crystallisation from a fairly dilute solution in acetone at 0° for several days) was not followed in the form now recommended, which was however employed in the third case (pig perinephric fat).

TABLE 113. *TYPICAL RESOLUTIONS OF FATS INTO GROUPS BY CRYSTALLISATION FROM ACETONE*

(a) *Ox Depot Fat* (S. Paul)

About 1 kg. of the fat was subjected to systematic crystallisation from acetone at 0° or room temperature as follows:

(i) The fat (in three portions for convenience) was dissolved in acetone (5 c.c. per g. of fat) and kept at room temperature overnight; after filtering the separated fat the solution was then cooled at 0° overnight and a further fraction of fat separated:

Fat Taken	Separated at Room Temperature			Separated at 0°			Left in Solution at 0°		
g.	No.	g.	I.V.	No.	g.	I.V.	No.	g.	I.V.
350	A_1	102	22·8	B_1	130	35·7	C_1	*118*	*56·3*
350	A_2	95	16·9	B_2	161	42·2	C_2	*94*	*57·6*
325	A_3	96	19·3	B_3	142	41·6	C_3	*87*	*57·6*

(ii) Corresponding fractions were then united and further crystallised as shown in the scheme below:

Fractions Crystallised		Conditions of Crystallisation			Separated Fat			Fat Left in Solution		
Nos.	g.	Acetone (c.c. per g. Fat)	Temp.	Time (Hr.)	No.	g.	I.V.	No.	g.	I.V.
$A_1+A_2+A_3$	293	3:1	Atmospheric	16	A_4	*244*	*15·9*	A_5	49	41·1
$B_1+B_2+B_3$	433	5:1	0°	6	B_4	*347*	*37·1*	(further 16 hr. at 0°)		
			0°	16	B_5	27	40·4	B_6	*59*	*55·3*
A_5+B_5	76	5:1	0°	6	D_1	*66*	*40·6*	D_2	*10*	*53·8*

The eight fractions (A_4, B_4, B_6, D_1, D_2, C_1, C_2, C_3) finally obtained were then assembled into three groups of similar I.V. as follows:

No.	g.	Per Cent. (Wt.)	I.V.	No.	g.	I.V.
A	244	23·8	15·9	A_4	244	15·9
B	413	40·3	37·5	B_4	347	37·1
				D_1	66	40·6
C	368	35·9	57·4	C_1	118	56·3
				C_2	94	57·6
				C_3	87	57·6
				B_6	59	55·3
				D_2	10	52·8

(b) *Cow Milk Fat* (S. Paul)

Nearly 2½ kg. of the fat were worked up in portions of 300 g. or 600 g. at a time. In the first trial (series A_1, etc.), crystallisation was first carried out at room temperature overnight, and the filtrate then left at 0° overnight (as in the ox depot fat, (*a*), above); but in the subsequent cases the order was reversed (initial crystallisation at 0° overnight, the deposited glycerides being recrystallised at room temperature overnight). The details were as follows:

(i) 302 g. milk fat in acetone (5 c.c. per gram fat) at room temperature overnight gave:

A_1, *31·1 g.* (*I.V. 25·7*) and left in solution B_1, 270·9 g.
B_1, 270·9 g. in acetone (5 c.c. per gram fat) at 0° overnight gave:
C_1, 77·7 g. (I.V. 32·0) and left in solution D_1, *193·2 g.* (*I.V. 55·2*).
C_1, 77·7 g. (I.V. 32·0) in acetone (3 c.c. per gram fat) at room temperature overnight gave:
E_1, *24·9 g.* (*I.V. 24·0*) and left in solution F_1, *52·8 g.* (*I.V. 36·4*).

(ii) The remainder of the milk fat was crystallised first at 0° overnight (3 c.c. acetone per gram fat).

FAT TAKEN	SEPARATED AT 0°		LEFT IN SOLUTION AT 0°		
G.	No.	G.	No.	G.	I.V.
611·1	A_2	233·0	B_2	*378·1*	*56·0*
607·3	A_3	216·7	B_3	*390·6*	*55·7*
623·8	A_4	235·0	B_4	*388·8*	*56·1*
306·6	A_5	104·0	B_5	*202·6*	*54·3*

Fractions A_2–A_5 were recrystallised from acetone (3 c.c. per gram fat) at room temperature overnight :

FRACTIONS RECRYSTALLISED		SEPARATED AT ROOM TEMPERATURE			LEFT IN SOLUTION AT ROOM TEMPERATURE		
No.	G.	No.	G.	I.V.	No.	G.	I.V.
A_2	233·0	G_1	*71·9*	*21·3*	H_1	*161·1*	*37·3*
A_3	216·7	G_2	*71·7*	*21·6*	H_2	*145·0*	*35·3*
A_4	235·0	G_3	*63·9*	*20·7*	H_3	*171·1*	*34·6*
A_5	104·0	G_4	*32·6*	*20·3*	H_4	*71·4*	*35·7*

The fractions A_1, E_1, G_1–G_4, F_1, H_1–H_4, D_1, and B_2–B_5, were then assembled into the following groups :

No.	G.	PER CENT. (WT.)	I.V.	No.	G.	I.V.
A	296·1	12·1	21·5	A_1	31·1	25·7
				E_1	24·9	24·0
				G_1	71·9	21·3
				G_2	71·7	21·6
				G_3	63·9	20·7
				G_4	32·6	20·3
B	601·4	24·5	36·8	F_1	52·8	36·4
				H_1	161·1	37·3
				H_2	145·0	35·3
				H_3	171·1	34·6
				H_4	71·4	35·7
C	1553·3	63·4	55·2	D_1	193·2	55·2
				B_2	378·1	56·0
				B_3	390·6	55·7
				B_4	388·8	56·1
				B_5	202·6	54·3

(c) *Pig Perinephric Fat* (W. H. Pedelty)

(i) About 1·2 kg. of the fat were crystallised, first from acetone (5 c.c. per gram of fat) at 0° for three days :

FAT TAKEN	SEPARATED AT 0°		LEFT IN SOLUTION AT 0°		
G.	No.	G.	No.	G.	I.V.
404·0	A_1	207·2	C_1	*196·8*	*72·9*
405·9	A_2	231·5*	C_2	*174·4**	*74·7*
412·0	A_3	214·4	C_3	*197·6*	*73·8*

(ii) Fractions A_1, A_2, A_3 recrystallised from acetone at room temperature overnight as follows :

FRACTIONS CRYSTALLISED		ACETONE USED (C.C. PER G. FAT)	SEPARATED AT ROOM TEMPERATURE			LEFT IN SOLUTION AT ROOM TEMPERATURE		
No.	G.		No.	G.	I.V.	No.	G.	I.V.
A_1	207·2*	5:1*	A_{12}	138·5*	—	B_1	68·7*	43·5
A_{12}	138·5	10:1	D_1	*92·7*	*22·8*	B_{12}	45·8	45·5
A_2	231·5	10:1	D_2	*73·8*	*20·1*	B_2	157·7	42·0
A_3	214·4	10:1	D_3	*86·3*	*21·4*	B_3	128·1	39·4

* In these instances the acetone used was slightly moist : the effect is evident.

TABLE 113. *TYPICAL RESOLUTIONS OF FATS INTO GROUPS BY CRYSTALLISATION FROM ACETONE—continued*

(iii) Fractions B_1 and B_{12}, also B_2 and B_3, were united and crystallised from acetone (10 c.c. per g.) at 0° for 3–4 days :

Fraction Crystallised		Separated at 0°			Left in Solution at 0°		
Nos.	G.	No.	G.	I.V.	No.	G.	I.V.
B_1+B_{12}	114·5	E_1	*97·7*	*36·8*	F_1	*16·8*	*62·0*
B_2+B_3	285·8	E_2	*237·4*	*36·3*	F_2	*48·4*	*62·1*

(iv) Fractions F_1 and F_2 were united and recrystallised from acetone (5 c.c. per g.) at 0° for 2 days, but gave little further separation (23·8 g. at I.V. 54·9 insoluble, and 41·3 g. at I.V. 66·1). It was therefore decided to treat these (reunited) as a separate small fraction of the fat.

The fractions C_1, C_2, C_3, D_1, D_2, D_3, E_1, E_2, F_1, F_2 were accordingly assembled into the following four groups of similar iodine value :

No.	G.	Per Cent. (Wt.)	I.V.	No.	G.	I.V.
A	252·8	20·7	21·5	D_1	92·7	22·8
				D_2	73·8	20·1
				D_3	86·3	21·4
B	335·1	27·4	36·8	E_1	97·7	36·8
				E_2	237·4	36·3
C	65·2	5·3	62·1	F_1	16·8	62·0
				F_2	48·4	62·1
D	568·8	46·6	73·8	C_1	196·8	72·9
				C_2	174·4	74·7
				C_3	197·6	73·8

(*d*) PRELIMINARY SEPARATION OF LIQUID FATS BY CRYSTALLISATION FROM ACETONE AT LOW TEMPERATURES

The procedure described in the preceding pages has been extended to more unsaturated fats by employing temperatures down to −50° for the crystallisations. The technique is of course the same as in the similar separation of the mixed saturated and unsaturated acids of a fat (this Chapter, pp. 471–474) and needs no additional description.

As in the preceding case of crystallisation at or above 0°, it has been found best [37c, 38] to commence the crystallisations at the lowest temperature to be employed, and to recrystallise the separated solids at progressively higher temperatures, rather than to commence at the highest temperature and cool the successive filtrates to increasingly lower temperatures. The approach to equilibrium between deposited solids and solution is even slower in the case of mixed glycerides than in that of the corresponding mixed fatty acids (*cf.* p. 472).

It is not of course possible as a rule to do more than determine the component acids of each group of mixed glycerides separated from the more unsaturated fats, but when adequate preliminary crystallisation has been achieved this often suffices to indicate the probable proportions of the chief component glycerides in each fraction (*cf.* Chapter VI, pp. 242, 243).

The application of this method to olive,[37a] cottonseed,[37b] and herring oils [38] is illustrated in Table 114. In the olive and cottonseed oils the crystallisations were carried out downwards from −10°, and a somewhat complex series of recrystallisations of intermediate fractions and filtrates was necessary to obtain the desired degree of resolution. The herring oil was crystallised from −40° upwards by the method recommended above, which proved much simpler and more effective, and also permitted the most unsaturated portions to be isolated first and dealt with, with minimum delay and exposure to oxidation. In order to indicate the varying composition of the groups of mixed glycerides, the percentage composition (molar) of the component acids in each group has been added.

TABLE 114. *TYPICAL RESOLUTIONS OF FATS BY CRYSTALLISATION FROM ACETONE AT LOW TEMPERATURES*

(a) *Olive Oil* (L. Maddison)

A Turkish olive oil (about 500 g.) was crystallised from acetone (5 c.c. per gram of oil) at −10° for several days. The soluble portion was crystallised from acetone (10 c.c. per gram) at −15°, and this process repeated on each soluble fraction at −20° and at −25°. Finally, the portion left in solution in acetone (10 c.c. per gram) at −25° was recrystallised from acetone (4 c.c. per gram) at −25°.

The following six fractions were thus obtained :

	A	B	C	D	E	F
Weight (g.)	40·3	116·9	100·9	115·1	82·0	44·5
Iodine value	67·9	67·8	79·0	85·1	94·4	100·7
Glycerides (mol. per cent.)	8·1	23·6	20·3	23·0	16·3	8·7
Component acids (mol. per cent.)						
Myristic	—	0·5	1·7	0·6	2·7	3·8
Palmitic	22·9	20·3	10·0	8·5	5·1	3·9
Stearic	4·8	3·7	2·1	0·4	—	—
Arachidic	—	1·1	0·2	—	—	—
Hexadecenoic	2·5	1·5	1·0	2·3	3·2	3·7
Oleic	66·2	70·3	80·8	81·1	79·0	73·7
Linoleic	3·6	2·6	4·2	7·1	10·0	14·9

(b) *Cottonseed Oil* (L. Maddison)

(i) The oil (610·6 g., iodine value 105·0) was crystallised from acetone (3 c.c. per gram) at −10° for 5 days, when it deposited 102·1 g. of solids ; these, on recrystallisation from acetone (5 c.c. per gram) at 20° for 18 hours gave 4·9 g. (fraction A) of solids and left 97·2 g. in solution.

(ii) The oil (508·5 g.) from the original filtrates was crystallised from acetone (5 c.c. per gram) at −30°, when 113·9 g. were left in solution, recovered, and recrystallised from acetone (5 c.c. per gram) at −35°, when a most soluble fraction (F) of 66·9 g. was obtained.

(iii) The 97·2 g. of oil from the filtrates of A, the 395·6 g. from the crystallisation at −30°, and the 47·0 g. from the crystallisation at −35°, were submitted to many more crystallisations at −10°, −20°, and −30°, intermediate deposits or filtrates of similar iodine value being in several instances combined for further crystallisation (full details are given in the original paper [37b]).

Finally, six fractions were obtained with the following properties :

	A	B	C	D	E	F
Weight (g.)	4·9	86·1	197·4	62·4	192·9	66·9
Iodine value	38·3	57·0	97·0	107·9	124·7	134·0
Glycerides (mol. per cent.)	0·8	14·5	32·5	10·2	31·3	10·7
Component acids (mol. per cent.)						
Myristic	—	3·5	3·2	1·6	2·0	0·8
Palmitic	68·4	53·8	27·5	22·3	12·7	8·2
Stearic	1·5	3·1	1·9	—	—	—
Arachidic	—	1·3	0·9	—	—	—
Hexadecenoic	—	2·0	1·2	2·7	2·7	4·3
Oleic	18·6	15·4	24·0	25·7	23·7	22·2
Linoleic	11·5	20·9	41·3	47·7	58·9	64·3

TABLE 114. *TYPICAL RESOLUTIONS OF FATS BY CRYSTALLISATION FROM ACETONE AT LOW TEMPERATURES—continued*

(c) *Icelandic Herring Oil* (O. B. Bjarnason and M. L. Meara)

In this case the oil (616·4 g., iodine value 140·0) was crystallised first from acetone (5 c.c. per gram) at −40°, when 66·2 g. (iodine value 207·6) was left in solution; the deposited solids were recrystallised from acetone at −40° when a further 55·4 g. (iodine value 196·1) was left in solution. These soluble portions were united to form fraction E.

The solids deposited in the second crystallisation at −40° were crystallised next from acetone at −30°, and the process repeated on the deposited solids at −10°, and similarly at 0° (using 5 c.c. acetone per gram of fat throughout). Five fractions were thus obtained: A (insoluble at 0°), B (soluble at 0°, insoluble at −10°), C (soluble at −10°, insoluble at −30°), D (soluble at −30°, insoluble at −40°), and E (soluble at −40°).

	A	B	C	D	E
Weight (g.)	53·3	77·0	68·5	75·0	121·6
Iodine value	59·3	83·6	122·3	148·8	202·4
Glycerides (mol. per cent.)	13·7	19·7	17·4	19·0	30·2
Component acids (mol. per cent.)					
Lauric	—	—	—	0·2	0·1
Myristic	14·9	12·1	8·1	7·4	5·2
Palmitic	24·4	17·2	14·5	10·9	5·6
Stearic	2·6	1·5	1·0	—	—
Arachidic	0·5	0·1	—	—	—
Unsaturated C_{14}	0·9(−2·0H)	1·5(−2·0H)	1·3(−2·0H)	1·7(−2·0H)	1·8(−2·0H)
,, C_{16}	4·9(−2·0H)	10·3(−2·0H)	12·9(−2·4H)	15·5(−2·3H)	17·9(−2·6H)
,, C_{18}	12·4(−2·3H)	16·1(−2·7H)	20·5(−3·1H)	21·4(−4·0H)	24·6(−4·3H)
,, C_{20}	15·5(−2·6H)	21·2(−3·1H)	25·2(−5·1H)	25·9(−5·9H)	27·9(−7·2H)
,, C_{22}	23·9(−2·5H)	20·0(−2·9H)	16·5(−3·5H)	17·0(−5·0H)	16·6(−6·6H)
,, C_{24}	—	—	—	—	0·3(−3·8H)

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